AN EXTENSION OF THE ANDERSON MODEL

AS A MODEL FOR MIXED VALENCE RARE EARTH MATERIALS.

By

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Preface

The work described in this dissertation was conceived and carried out under the supervision of Professor P. W. Anderson at Princeton University, New Jersey, over the period 1976-77, drawing on experience gained during an apprenticeship of twenty months graduate work with him at the Cavendish Laboratory, Cambridge, and a summer as a visitor at Bell Laboratories.

Chapter one, and chapter two, sections 2.1 to 2.4, are brief reviews of the mixed valence problem and the current state of knowledge of the properties of the Anderson and Kondo models. Since these are potentially vast topics, these reviews reflect my personal prejudices as to which aspects are most important. To the best of my knowledge, the material presented from section 2.5 onwards is original; those places where it draws on previous work are indicated by references in the text to the earlier authors.

The seminal idea that started this work was the suggestion by Phil Anderson that screening effects from $\ell \neq 3$ scattering channels of the rare-earth atoms might be important components of the eventual explanation of the mysterious properties of the mixed valence rare-earth compounds, and also that the techniques he developed in conjunction with my predecessors Gideon Yuval and John Armytage could prove useful in this context.

I wish to express my gratitude to my Supervisor Phil Anderson for his support and guidance during my graduate studies, and also for sharing with me his insight into which aspects of a problem are physically important.

I must also express my deep appreciation to my good friend Marcia Brubeck, who generously donated her skills to the task of transforming vast piles of incomprehensible and illegible manuscript into the semblence of a thesis in the face of a rapidly approaching deadline.

For financial support, I am indebted to the taxpayers of Great Britain for an SRC studentship held at the Cavendish Laboratory 1973-75, and a NATO studentship held abroad at Princeton University 1975-76. Finally, I was supported by a contract with Bell Laboratories program of research in theoretical physics for the period 1976-77 at Princeton. While at Princeton, travel funds and other overheads, such as the support of my Xerox habit, were provided by NSF contract DMR 76 00866 A01.

I must also acknowledge the hospitality of the Aspen Center for Physics, where I put the final touches to this thesis.

This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration. Furthermore, I hereby declare that my dissertation entitled "An extension of the Anderson model as a model for mixed valence rare-earth materials" is not substantially the same as any that I have submitted for a degree, diploma or other qualification at any other University. I further state that no part of my dissertation has already or is being concurrently submitted for any such degree, diploma or other qualification.

[redacted]

F. D. M. Haldane,

Aspen, Colorado, July 15, 1977.

Note on the Amended Version .

Following the oral examination of this thesis on October 7 th 1977 by Professor V. Heine of the Cavendish and Dr. D. M. Edwards of Imperial College, certain amendments have been made. In particular the discussion of the effects of coupling to a "slow" phonon field (chapter four) has been extended, and the evaluation of the perturbation series discussed in section 5.3 has been described in detail in an appendix to chapter five. Other improvements are the discussion of Langreth's Fermi liquid theorem in section 2.5 and 2.6 ; the interpretation of the scaling equations (section 6.4) has also been modified, and the arguments presented in what is hopefully a more physical and less formal form.

[redacted]

F. D. M. Haldane
Grenoble, France,
January 15th, 1978.

Publications:

Some material from this thesis has been published and may be found as follows:

"Hartree-Fock study of the Anderson model coupled to a boson field; mixed valence states"
F. D. M. Haldane, Phys. Rev. B15, 281 (1977).

"New model for the mixed-valence phenomenon in rare-earth materials"
F. D. M. Haldane, Phys. Rev. B15, 2477 (1977).

"Scaling theory of the asymmetric Anderson model"
F. D. M. Haldane, Phys. Rev. Lett. 40, 416 (1978).

ABSTRACT.

The Phenomenon of mixed valence in certain rare-earth compounds is briefly reviewed. The Kondo-like behaviour of the resistivity of mixed valence coumpound compounds such as $CeAl_3$ suggests that there is little coherence between rare-earth atoms except at very low temperatures, and that a model of a single rare-earth impurity in a metal may be usefully studied. The configurational instability regime ($E_d \simeq 0$) of the Anderson model of a magnetic impurity in a metal is a natural choice for such a study; however it is pointed that on physical grounds it must be generalised to include dynamic screening processes; coupling of valence fluctuations to the lattice is also included as a linear coupling to the phonon field. The limit in which these phonon frequencies are slow compared to electronic relaxation times is treated in mean-field theory, and two degenerate Hartree-Fock states with different valence may be found. Reincluding phonon dynamics with the Born-Oppenheimer approximation, it is found that this implies that there are slow valence fluctuations, controlled by tunnelling of the Phonon field between the two degenerate minima of the effective potential.

A perturbation expansion in Δ, the hybridisation, is developed for the Anderson model and its generalisations. It is noted that, provided it is large, the conduction bandwidth is not relevant in the unscreened case , and the limit of infinite bandwidth is the most convenient to treat. By comparison of the susceptibility expansion with that for the Kondo model, the Kondo temperature of the local moment regime is found to be proportional to $(U\Delta)^{\frac{1}{2}}\exp(E_d(E_d+U)/(2\Delta U/\pi))$ (corresponding to the Schrieffer-Wolff value for $J\rho$ and $(-E_d(E_d+U))^{\frac{1}{2}}$ for D); the precise proportionality coefficient may also be obtained. The eventual crossover to a non-magnetic state as E_d is changed from the "symmetric" value of $-\frac{1}{2}U$ is investigated by a scaling technique, as it is associated with logarithmic terms in the pertubation expansion; the

criterion for the existence of a local moment regime and spin-compensated Kondo ground states is found to be $T_K \ll \Delta$. When the above expression for T_K is of order Δ, the local moment description is never valid, and below a "valence fluctuation temperature" of order Δ the system condenses into a Fermi liquid with sustantially non-integral valence. Properties in this crossover region are found to depend solely on the scaling invariants Δ and $E_d^* = E_d + \Delta/\pi \ln(W/\Delta)$, where W is a high energy cutoff given by U or the conduction bandwidth, whichever is the smaller. The criterion for this mixed valence state is $|E_d^*|$ (not $|E_d|$) $\ll \Delta$. With the aid of the scaling theory, various crossovers of the properties of the system as a function of temperature are described.

The effects of screening and coupling to "fast" phonons on the mixed valence state are also examined by these scaling techniques, and are found to result in a renormalisation of Δ. In the case of electronic screening, this renormalisation is estimated to be negligeable in practice, but coupling to phonons, whether fast or slow, can potentially give rise to sustantially reduced "valence fluctuation temperatures"; however, the dependence of this on the model parameters is too sensitive for direct comparison with experiment to be reliable. The results are synthesised into a picture of the mixed valence state as a Fermi liquid state with a virtual bound state, possibly with substantially reduced width and weight as a result of coupling to phonons, at the Fermi level.

Dedicated to:

Phil Anderson,

whose model started it all,

and

Marcia Brubeck.

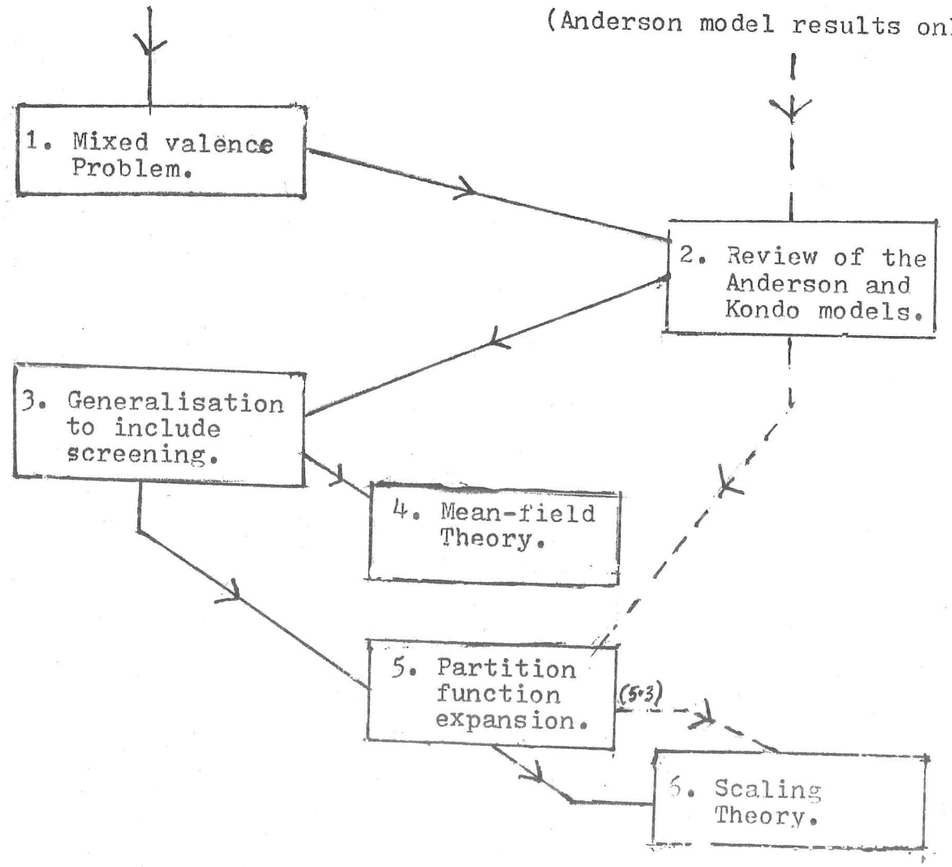
CONTENTS

A note on the structure of this thesis.

Each chapter is written so as to be as self-contained as possible; a list of references and any appendices are given at the end of each chapter. Except where experimental results are referred to, units of temperature and frequency are such that $k = \hbar = 1$.

Those interested only in the results on the standard Anderson model (without screening terms) should read only chapters 2, 5.1-5.3, and 6.

The relationship between chapters is shown below:



CHAPTER ONE

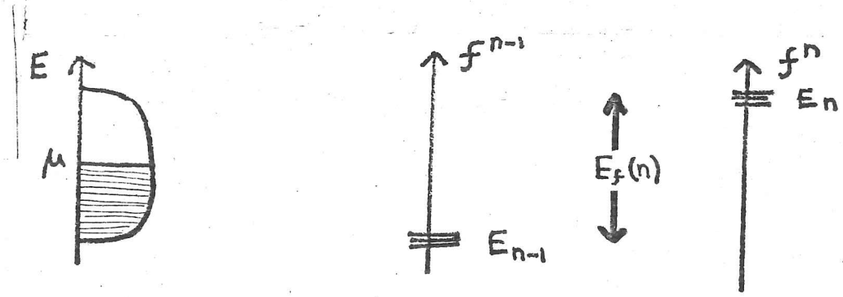
REVIEW OF THE MIXED VALENCE PROBLEM

1.1 Introduction

Characteristically, f-electrons in rare-earth materials do not take part in conduction processes. Intra-atomic interactions are so strong that a band picture cannot be applied to the f-electrons in a solid; as the f-orbitals are spatially highly localised inside the core region of the atom, not only are intra-atomic Coulomb matrix-elements greatly enhanced compared to those between, say, d-electrons, but matrix elements for hybridisation with orbitals on neighbouring atoms are also greatly reduced.

In this circumstance, the basic description of the f-electrons must be in terms of the electronic configurations of the free atom, with interactions between neighbouring atoms treated as a small perturbation. If the ground state configuration of the f-orbitals is singlet, they are effectively inert, and f-electrons play no role; if it has $J \neq 0$, the f-electrons will act as a lattice of Heisenberg spins, with small effective exchange couplings between sites generated by the weak hybridisation term. In such cases the f-orbitals are said to have 'integral valence.' Of course, formally even an infinitesimal hybridisation term will mix excited configurations of the free atom with different valences into the ground state, so technically the atom in a solid is always in a state of 'mixed valence'; however, in contrast to the case of s-, p- or d- orbitals, such admixture is usually extremely small. To all intents and purposes, these excited configurations occur as a consequence of the virtual processes that mediate the exchange interactions between the effective Heisenberg spins. The term 'mixed valence' is reserved for those special cases

where two configurations with different f-orbital valences are both present in significant amounts in the ground state, while the electronic state of the rare-earth atoms remains homogeneous throughout the solid.



(a) d-band (delocalised) (single-particle) density of states.

(b) f-orbital (localised) atomic configurational spectrum.

Fig. 1.1. Model of a rare-earth metal (see text).

Consider the following highly oversimplified model of a rare-earth metal (Fig. 1.1): the d-electrons are assumed to have completely delocalised into a conduction band which contains the Fermi level, while the f-electrons reside in isolated atomic orbitals on each site, with no hybridisation. The configurational spectrum of the f-orbital is simplified so all relevant configurations with the same valence are degenerate, and only the two valences f^{n-1}, f^n are energetically accessible. If the energy $E_f(n)$ of the configurational excitation $f^{n-1} + e \rightleftarrows f^n$ lies below the Fermi level, the ground state configuration will be f^n; if it is above, f^{n-1} is stable.

Figure (1.2) shows the effect of systematically increasing $E_f(n)$, while keeping the total charge constant. When $E_f(n)$ reaches the Fermi level, f-electrons begin to empty into the conduction band and the system goes into a state of 'mixed valence'; the chemical po-

tential μ tracks $E_f(n)$ until one electron per rare-earth atom has been transferred to the conduction band, and integral valence (f^{n-1}) of the f-orbitals again holds. When hybridisation is included, the configurational excitation will acquire a finite lifetime, and may be regarded as forming a very narrow 'f-band' in the single particle spectrum; however, this 'f-band' can only hold one electron per atom.

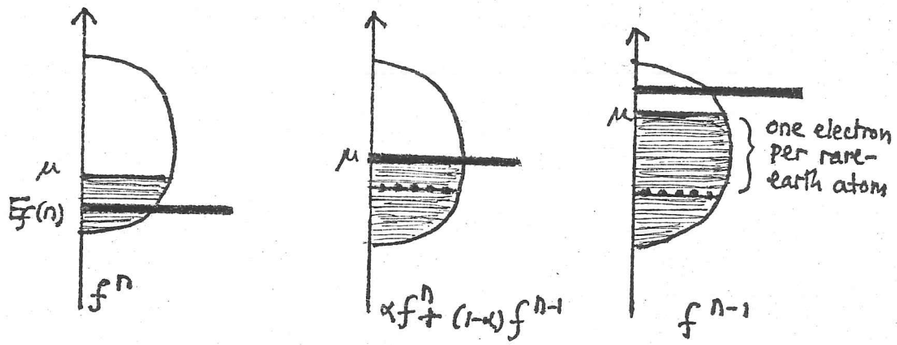


Fig. (1.2). Effect of varying $E_f(n)$.

If rare-earth materials are systematically studied, most will be in states of integral valence, as the energy level splittings between configurations with different valences are very large, and the probability that $E_f(n) \simeq \mu$ is small. Nevertheless, a few compounds should be found in the mixed-valence state, where the Fermi level is pinned to the configurational instability. Such materials will be distinguished by highly anomalous properties.

In some materials, for example Fe_3O_4, where two configurations Fe^{2+} and Fe^{3+} are present, the system stabilises itself by a structural change so the ions with different valences sit on two equivalent sublattices. Such systems are not in the mixed-valence state in the sense used here; the rare-earth materials under consideration are found to be spatially homogeneous.

The f-orbitals on each site have some amplitude for being in either valence state. This state is sometimes described as an 'interconfigurational fluctuation state' (ICF), where the 'fluctuations' are understood in the sense of a zero-point motion.

In a realistic model of the mixed valence state, many additional factors must be taken into consideration; for example, lattice size and conduction electron charge distribution around the rare-earth atom will be strongly coupled to valence fluctuations. The effect of such terms will be considered in detail later.

1.2 Some Characteristics of Mixed Valence Compounds

Extensive reviews of mixed valence (MV) compounds have been given by Varma (1976), Jayaraman et al. (1975), Maple and Wohlleben (1973) and Mott (1974). See also the proceedings of the recent Rochester conference (Parks, (1977)). An overview, stressing selected properties, will be given here.

The most widely studied MV rare-earth compounds are samarium chalcogenides, SmS, SmSe, SmTe (Jayaraman et al. (1975)), which change from semiconductors ($Sm^{2+} = 4f^6$) to MV metals (Sm^{2+}/Sm^{3+}) under the effect of pressure or alloying with the smaller ion, Gd^{2+}. Similar transformations occur in ytterbium chalcogenides ($Yb^{2+} = 4f^{14}/Yb^{3+}$) and TmTe($Tm^{2+} = 4f^{13}/Tm^{3+}$). These changes are isostructural, and accompanied by a ~10% decrease in volume. SmS is distinguished by the change being discontinuous, and strongly first order, leading to the dramatic 'black/gold explosive transition.' The change is continuous in the other compounds. Much work has been done on the investigation of the nature and thermodynamics of the transition (which is also a metal-insulator transition); this work will, however, be more concerned with the character of the MV metallic state itself, possibly best represented by such systems as cerium metal (Jayaraman (1965)), and the alloys $CeAl_2$, $CeAl_3$, $YbAl_2$, $YbAl_3$ (Buschow et al. (1970), Havinga et al. (1973)).

Three main effects indicate the presence of non-integral valence.

(a) Lattice constants of a particular rare-earth compound may be studied as the rare-earth is varied through the lanthanide series (Jayaraman et al.(1975)). In general MV compounds have anomalous lattice constants, lying between extrapolated estimates of their

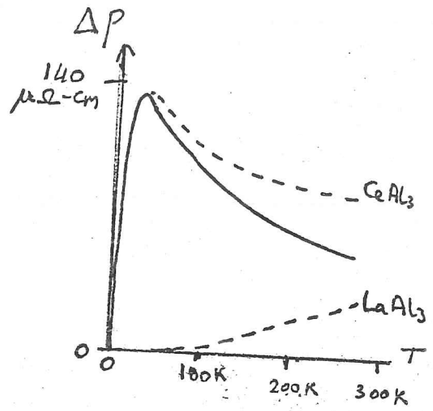
values for the pure +n and +(n-1) ionic states.

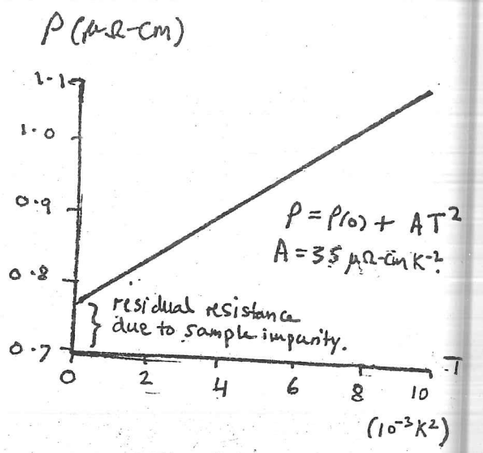
(b) Mössbauer shift studies (Cohen et al. (1970)), when a suitable isotope is available (e.g., Sm^{149}), probe the conduction electron density at the nucleus, and hence, through the screening interaction, the f-orbital valence. Studies show that MV compounds are homogeneous on a timescale of 10^{-10}s., but the line shift is intermediate between that found for pure f^n and f^{n-1} ionic configurations.

(c) X-ray photospectroscopy (XPS) spectra (Campagna et al. (1974)) take a 'snapshot' of the configuration of the rare-earth ion on a time scale of 10^{-18}s. Spectra of MV compounds show the unambiguous 'fingerprints' of two different valence states in the spectra. On the timescale of the experiment, the material resembles a random alloy of the two configurations.

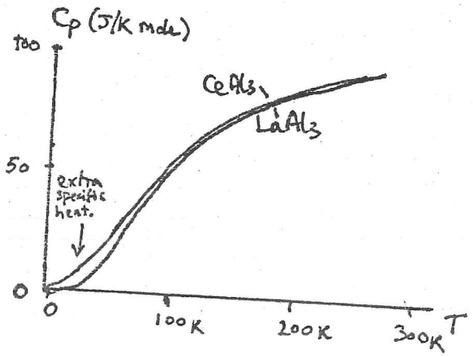
These three effects each allow an estimation of the mixing ratio f^{n-1}/f^n; and produce comparable results. They also define a timescale for valence fluctuations, usually estimated as 10^{-12}-10^{-13}s (corresponding to zero-point energies of a few meV). This behaviour has recently been directly tested (Holland-Moritz et al. (1977)) by diffuse neutron scattering on the MV compound $CePd_3$; a configurational lifetime of 1.8×10^{-13}s. is reported.

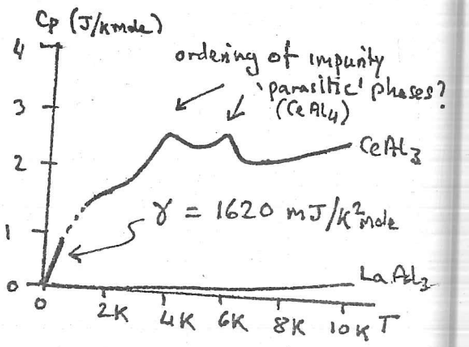
In most MV materials studied (compounds of Sm, Eu, Yb and Ce) one of the two configurations involved is a singlet, J=0. In that case a characteristic of the material is its failure to order magnetically, even if the proportion of J≠0 configuration dominates. This stands in dramatic contrast to normal rare-earth materials, which are strongly magnetic if J≠0. A striking example is the so-called 'dense Kondo system' $CeAl_3$, which has recently been studied down to



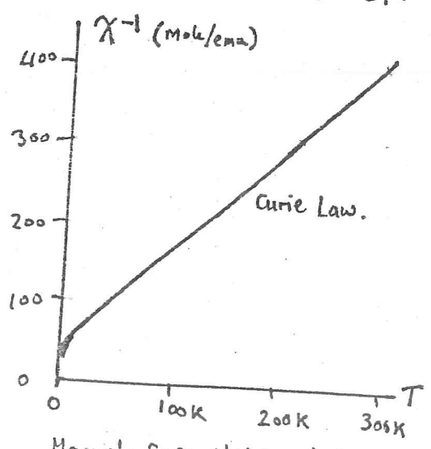


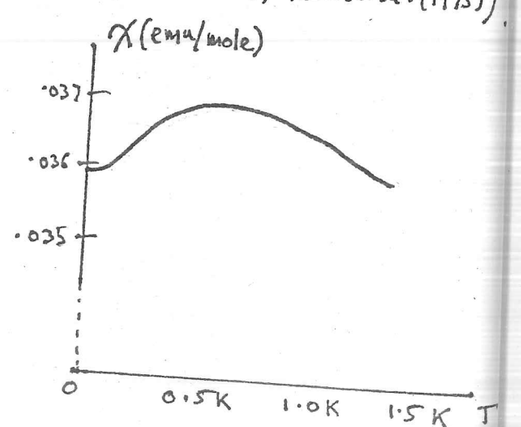
RESISTIVITY OF $CeAl_3$ (Buschow and Van Daal (1970), Andres et al. (1975)).





SPECIFIC HEAT OF $CeAl_3$ (Mahoney et al. (1974), Andres et al. (1975)).





Magnetic Susceptibility of $CeAl_3$. (Mader and Swift (1968), Andres et al (1975)).

Fig. (1.3). Properties of $CeAl_3$.

sufficiently low temperature to observe the limiting behaviour (Andres et al. (1975)). Though anomalous, like many other cerium compounds, the amount of Ce^{4+} (f^0) mixed in with Ce^{3+} (f^1) is undetectable (<5%). In spite of this, the properties of this material show that the mixed valence effect is involved. $CeAl_3$ may be usefully compared to $LaAl_3$, which is expected to be very similar except that the f-orbital is empty. The dramatic differences between the two materials may then be attributed to the f-electrons.

The resistivity, specific heat and susceptibility of $CeAl_3$ are shown schematically in Fig. (1.3). The most striking feature is the rise in excess resistivity over that of $LaAl_3$ as the material is cooled; at its maximum, around 40K, it is comparable to the unitarity limit of incoherent scattering by an $\ell=3$ virtual bound state on each lattice site (Andres et al. (1975)). Below 5K it drops off again, finally vanishing with a strong T^2 dependence, attributed by Mott (1974) to Baber scattering between 'heavy' particles in a narrow band, and 'light' particles in a wide band; using Baber's formula, Andres finds $T_f \simeq 3K$ for the narrow band.

The excess specific heat (Mahoney et al. (1974)) shows a Shottky-like anomaly around 40K; the features around 4-6K are probably impurity features (e.g., $CeAl_4$, always present in small quantitites, orders magnetically at 6K). Integration of the specific heat curves shows that the zero temperature entropy is much less than the $k\ln 2$ expected for a crystal electric field doublet (J=5/2 in a hexagonal field) (Andres (1975)), and possibly zero (Mahoney et al. (1974)). The limiting low temperature behaviour is linear, with a huge γ-coefficient corresponding to a Fermi gas with degeneracy temperature $T_f \simeq 25K$. The susceptibility measurements at low

temperatures show the Curie law giving way to a temperature independent value; if this is a Pauli susceptibility, $T_f \simeq 15K$.

The low temperature behaviour points to the ground state being a Fermi liquid with a narrow band of collective excitations right at the Fermi level.

The intermediate temperature behaviour is very reminiscent of the Kondo effect (see section 2.4) and $CeAl_3$ is sometimes described as a 'dense Kondo system.' The resistivity becomes so large that each rare-earth atom must be scattering incoherently. This naturally leads to the idea that this intermediate regime can be described by an ensemble of isolated 'impurity' rare-earth atoms in a metal. Only at still lower temperatures when coherence develops must account of interactions between rare-earth atoms be taken.

A phenomenological description might be as follows: as the temperature is lowered, the coupling of an isolated rare-earth impurity, which is close to configurational instability, to the conduction band of its host metal leads to the formation of a collective virtual bound state (VBS) (Friedel (1958)) at the Fermi level, and the resistivity rises. The first goal of a theoretical investigation should be to examine how this comes about. In an array of rare-earth atoms in a solid, the processes that give rise to VBS formation are usually forestalled by a phase transition to a magnetic state at a temperature T_N higher than that for VBS formation. MV materials may be characterised by having $T_{VBS} > T_N$; at lower temperatures, coherence among the VBS will develop, and a narrow band of collective excitations will form. The ground state may be characterised as a Fermi liquid with a large density of states at the Fermi surface, due to this collective band.

A very natural choice of impurity model for investigating the intermediate temperature region is the Anderson model (Anderson (1961)), which is reviewed in the following chapter.

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CHAPTER TWO

REVIEW OF THE ANDERSON MODEL AND RELATED MODELS

2.1 Physical Basis of the Anderson Model and Related Models

The Anderson model (Anderson (1961)) was proposed as a model of a transition metal impurity in a non-magnetic host metal, and used to study the conditions determining the presence or absence of a local magnetic moment on the impurity. These conditions were seen very clearly in the Hartree-Fock treatment of the model, and were successfully related to systematic variations of the occurrence and size of local moments with the position of the impurity in the transition metal series (Clogston et al. (1962)). Following the discovery (Kondo (1964)) that the related s-d or Kondo model (in which a free spin is exchange-coupled to a Fermi gas) was not as trivial as was first thought, and that higher order perturbation theory in the exchange coupling constant was infra red divergent as $T \to 0$, it was realised that the same effect was present in the Anderson model (Schrieffer and Wolff (1966)).

The apparent simplicity of these models, coupled with their apparent intractability, stimulated a vast literature (for a partial list, see Kondo (1969), Grüner and Zawadowski (1974)) of theoretical studies aimed at exposing the exact nature of the ground state, together with the extensive experimental study (see the review by Rizzuto (1974)) of dilute systems of magnetic impurities. The nature of the solution was clarified by the development of the Anderson-Yuval scaling theories (Anderson (1970); Anderson, Yuval and Hamann (1970)); finally Wilson (1975) developed the tools for the essentially exact numerical solution of the problem with his renormalisation group (RG) technique.

Like most successful models, the Anderson model is phenomenological in character. Its detailed derivation from first principles would be arduous, but might perhaps be achieved using Anderson's 'chemical

pseudopotential' formalism (Anderson (1969)) in which the wave functions of solids are constructed from the non-orthogonal localised wave functions of an 'atomic-like' pseudo-Hamiltonian. In any case, as the bulk of the interactions in the model are considered to have been removed by a Landau Fermi-liquid renormalisation technique, the numerical values of the parameters should not be identified literally with their apparent 'bare' or 'a priori' values. Despite this phenomenological nature of its parameters, the Anderson model has allowed deep insight into the behaviour of magnetic impurities.

The physical rationale behind the Anderson model is intuitively simple. A transition metal impurity, such as a gold atom, in an otherwise similar host such as copper, has the effect of adding an extra set of d-orbitals to the truncated Hilbert space of energetically available s-p wave functions making up the host conduction band. The conduction band Wannier function of the impurity atom is assumed to be much the same as that of the host atom it replaces.

Interactions between conduction electrons have been removed, and these particles are interpreted as Fermi-liquid quasi-particles. As the d-orbitals are physically much more localised in space than s or p orbitals, the Coulomb and exchange matrix-elements between d-electrons on the impurity atom are much larger than those between conduction electrons, and this extra interaction strength is explicitly included in the Hamiltonian.

A small hybridisation term allowing d-electrons to 'hop' into the conduction band, and vice versa, is included. This matrix element will be relatively small, as symmetry requires d-electrons to hop into the Wannier orbitals of neighbouring atoms only, not those of the impurity site itself, which have s or p symmetry about the impurity. As the d-orbital is very localised these matrix elements with orbitals

on neighbouring sites are very small.

The Hamiltonian is

$$H = \sum_{k\sigma} \varepsilon_k c^+_{k\sigma} c_{k\sigma} + \sum_{k\sigma} V_{km} c^+_{k\sigma} c_{m\sigma} + h.c. + H_d \qquad (2.1.1)$$

$$H_d = \sum_{m\sigma} E_d n_{m\sigma} + U \sum_{m\sigma \neq m'\sigma'} n_{m\sigma} n_{m'\sigma'} - J S_d^2 - K L_d^2 + \lambda \vec{L}_d \cdot \vec{S}_d \qquad (2.1.2)$$

Various intra-atomic exchange terms to model the configurational spectrum of the d-orbital may be included. Here $c_{m\sigma}$ is the impurity orbital creation operator, and $\vec{S}_d$, $\vec{L}_d$ are the impurity orbital spin and orbital angular momentum operators.

As d-electrons will only hop to orbitals with the same point symmetry, a basis set of spherical waves (or, more generally, representations of the appropriate point group) centred on the impurity site is most convenient for describing the conduction electrons; since in this case only $\ell=2$ spherical waves of the conduction band will hybridise with the d-orbitals, other ℓ-values may be considered to have been implicitly omitted from (2.1.1).

The interaction with the conduction band is completely determined by the spectral density

$$\Delta(\omega) = \pi \sum_k |V_{km}|^2 \delta(\omega - \varepsilon_k) \qquad (2.1.3)$$

The resonance width Δ ($= \Delta(0)$, the chemical potential μ being taken as zero) of an impurity level at the Fermi level is the characteristic measure of the hybridisation strength. For $\Delta \ll U$, J etc., the impurity will at almost all times be in the lowest energy state of the 'free atom,' ($\Delta=0$); the effect of finite Δ is to allow resonant scattering of conduction electrons during which the impurity is virtually excited to other valences. In the strong hybridisation limit, $\Delta \gg U,J$, the d-electrons become highly delocalised and the effects of the interactions are weak, and can be treated by perturbation theory in U.

A more subtle property of the model is the difference between Δ small, and the atomic limit, $\Delta=0$. For finite Δ, zero U, J, etc., the ground state of the model, now a non-interacting Fermi gas, is clearly a singlet. This remains true if infinitesimal interaction terms are 'switched on.' The system is essentially finite or 'zero dimensional,' and in an analogous fashion to the effect of finite temperature on low dimensional systems, the quantum fluctuations associated with finite Δ prevent any sharp discontinuities or 'phase transitions' as the interaction strengths U, J are increased; hence the ground state of (2.1.1) is always a singlet for finite hybridisation. In contrast, for $\Delta=0$, the ground state may be degenerate, corresponding to a lowest energy configuration of H_d with non-zero angular momentum; in that case the ground state for finite Δ has a different symmetry from that at zero Δ. Since the effects of coupling a finite system to a heat bath at finite temperature prevents any discontinuities, such problems are limited to zero temperature, where they cause an infra-red divergence of perturbation theory in Δ as $T \to 0$. This divergence is symptomatic of the Kondo effect (dealt with later) and is what makes the treatment of this model both difficult and challenging enough to have inspired so much theoretical effort in the last decade.

The simplest and most widely studied version of the model, which will be discussed more fully in the next section, is the 'non-degenerate' case where the set of impurity d-orbitals $c_{m\sigma}$ is replaced by an s-like single orbital $c_{d\sigma}$. Only the Coulomb term U in (2.1.2) need be retained. Insofar as the Kondo effect is concerned, it is likely that this simpler case is qualitatively similar to the full degenerate orbital model.

The Anderson model has found other interpretations besides its original one as a magnetic impurity. In particular (Newns (1969)) it has been used to model the chemisorption of gas molecules on a metal surface. In that case the extra orbital represents a molecular orbital on the gas molecule, which hybridises with the metal substrate orbitals, yielding a model of chemical bonding to the surface.

Two related models must now be mentioned. The Wolff model (Wolff (1961)) is a single-site precursor of the Hubbard model (Hubbard (1964)): an extra interaction term is included at a single site in a metal.

$$H = \sum_{k\sigma} \varepsilon_k c^+_{k\sigma} c_{k\sigma} + U n_{o\uparrow} n_{o\downarrow} \qquad (2.1.4)$$

$n_{o\sigma}$ is the occupation number operator of the impurity-site Wannier function. For large U this model also describes the formation of a local moment; though their physical interpretations (and hence the interpretation of such properties as impurity specific heat, transport properties, etc.) are different, the Wolff model with a non-degenerate band, and the non-degenerate Anderson model are in fact formally equivalent through a canonical transformation. The form (2.1.4) is appropriate for perturbation theory in the small U/Δ limit.

The other related model is the Kondo or s-d model (Kondo (1964)), where a free spin interacts with a Fermi gas.

$$H = \sum_{k\sigma} \varepsilon_k c^+_{k\sigma} c_{k\sigma} - J \vec{S} \cdot \tfrac{1}{2} \sum_{\sigma\sigma'} \left(c^+_{o\sigma} \vec{\sigma}_{\sigma\sigma'} c_{o\sigma'} \right) \qquad (2.1.5)$$

For a certain range of its parameters, the non-degenerate Anderson model may be transformed to the $S = \frac{1}{2}$ weak-coupling antiferromagnetic (negative J) Kondo model. Care is needed in relating $S > \frac{1}{2}$ Kondo models to degenerate Anderson models: the Pauli matrices $\vec{\sigma}$ must be replaced by full $\vec{J} = \vec{L} + \vec{S}$ matrices, and the multiplicity of impurity site Wannier

functions taken into account. Little work has been done on such $S > \frac{1}{2}$ models. Mattis (1967) has shown that with the separable potential form of (2.1.5), the spin quantum number of the ground state is $S - \frac{1}{2}$ for the antiferromagnetic case (J negative), (and $S + \frac{1}{2}$ for J positive); for $S > \frac{1}{2}$, this is clearly in contradiction with the singlet ground state of the Anderson model. Okada and Yosida (1973) have studied the degenerate Anderson model in more detail, and derived equivalent Kondo-like models.

2.2 Formal Structure of the Non-Degenerate Anderson Model

Specialising to the non-degenerate Anderson model, it may be seen to be one of the simplest but decidedly non-trivial interacting fermion systems. Consider the general Hamiltonian, in an unspecified ba

$$H = \sum_{ij\sigma} h_{ij}\, a^{+}_{i\sigma} a_{j\sigma} + \tfrac{1}{2} \sum_{ijkl\,\sigma\sigma'} V_{ijkl}\, a^{+}_{i\sigma} a^{+}_{j\sigma'} a_{k\sigma'} a_{l\sigma} \qquad (2.2.1)$$

The choice of a separable interaction potential leads to the Anderson model:

$$V_{ijkl} = U v_i^* v_j^* v_k v_l \;; \quad \sum_i |v_i|^2 = 1 . \qquad (2.2.2)$$

Define the operator

$$c_{d\sigma} = \sum_i v_i\, a_{i\sigma} \qquad (2.2.3)$$

and choose a basis to diagonalise h_{ij} ;

the Pauli principle prevents particles of the same spin from interacting

$$H^{\circ} = \sum_{i\sigma} \varepsilon_i a^{+}_{i\sigma} a_{i\sigma} \;; \; H = H^{\circ} + U n_{d\uparrow} n_{d\downarrow} . \qquad (2.2.4)$$

The model is now in Wolff form, the natural form for small U. For large U, a new basis is appropriate; define E_d, V, and ψ_σ by:

$$[H^{\circ}, c^{+}_{d\sigma}] = E_d\, c^{+}_{d\sigma} + V \psi^{+}_{\sigma}$$
$$\{c_{d\sigma}, \psi^{+}_{\sigma}\} = 0 \quad . \qquad (2.2.5)$$

Furthermore

$$V \psi_\sigma = \sum_k V_{kd}\, c_{k\sigma} \quad , \qquad (2.2.6)$$

where

$$[H^{\circ}, c^{+}_{k\sigma}] = \varepsilon_k c^{+}_{k\sigma} + V^{*}_{kd}\, c^{+}_{d\sigma} \quad . \qquad (2.2.7)$$

Finally, in this new basis:

$$H = \sum_{k\sigma} \varepsilon_k c^{+}_{k\sigma} c_{k\sigma} + E_d \sum_{\sigma} n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + \sum_{k\sigma} V_{kd}\, c^{+}_{k\sigma} c_{d\sigma} + \text{h.c.} \qquad (2.2.8)$$

In the 'atomic limit', $V_{kd} = 0$, (2.2.8) is in diagonal form, and the behaviour of the ground state as a function of the parameters E_d and U is shown in Fig. (2.1). The case $E_d = -\frac{1}{2}U$ is called the 'symmetric model', indicating that the Hamiltonian has particle-hole symmetry .

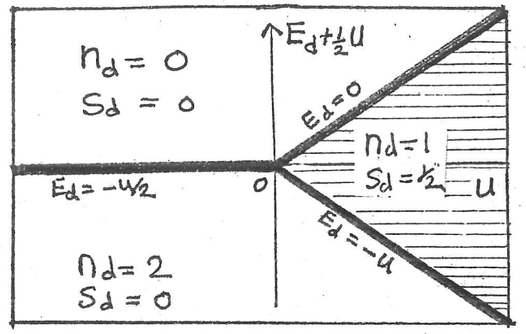

Fig. (2.1).
Ground state of the atomic limit ($\Delta=0$) of the Anderson model as a function of the parameters ($E_d + \frac{1}{2}U$), U. Magnetic region is shaded.

Of particular interest is the sector $U>0$, $0>E_d>-U$, where the ground state is degenerate, and has non-zero spin $S=\frac{1}{2}$.

The hybridisation with the conduction band is characterised by the spectral density $\Delta(\omega)$, given by (2.1.3). If the model is used in the context of chemisorption, as mentioned in the previous section, it may be important to retain a realistic band structure; however, in the study of the magnetic impurity it is often convenient to make the choice $\Delta(\omega)=\Delta$, constant. If this is translated into Wolff model form (2.2.4) this choice corresponds to a Lorentzian density of states:

$$\rho(\omega) = \frac{1}{\pi} \frac{\Delta}{(\omega - E_d)^2 + \Delta^2} \quad . \qquad (2.2.9)$$

It must, however, be noted that this choice corresponds to an infinite bandwidth for the conduction band of the Anderson model, and hence a divergent but subtractable ground state energy that depends on Δ, necessitating care in formulation perturbation expansions in that quantity. This problem is dealt with in chapter five.

When the hybridisation Δ is included, the model will exhibit complicated behaviour near the regions of configurational crossover shown in Fig. (2.1). Away from these regions, however, transformations to a simpler effective Hamiltonian are available. These may simply

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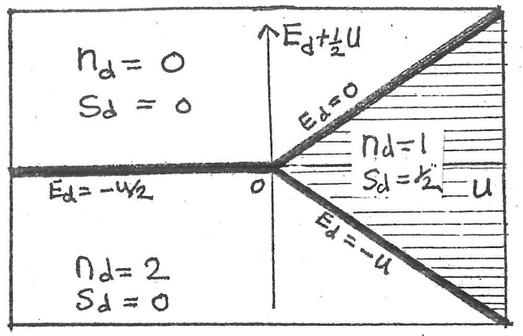

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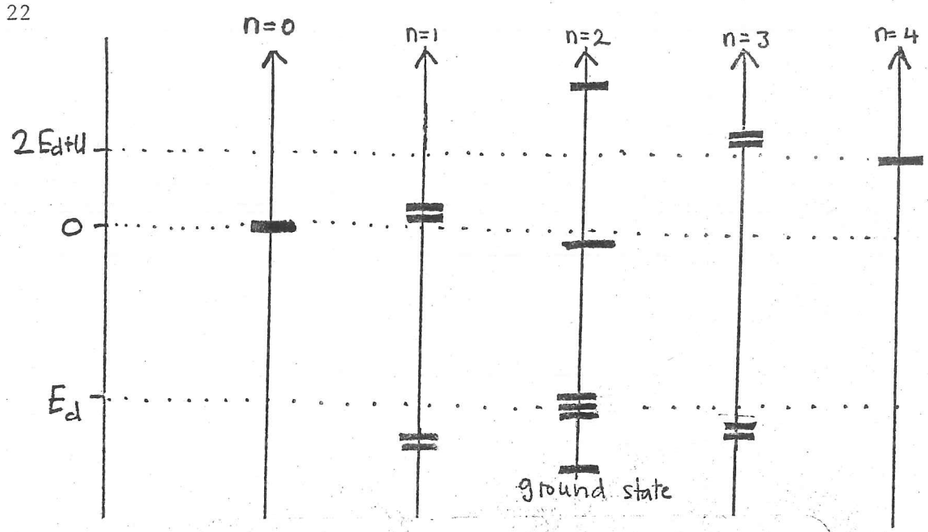


n=0: $\omega = 0$

n=1: $\begin{vmatrix} E_d-\omega & V \\ V & 0-\omega \end{vmatrix} = 0$ (doublet)

n=3: $\begin{vmatrix} 2E_d+U-\omega & V \\ V & E_d-\omega \end{vmatrix} = 0$ (doublet)

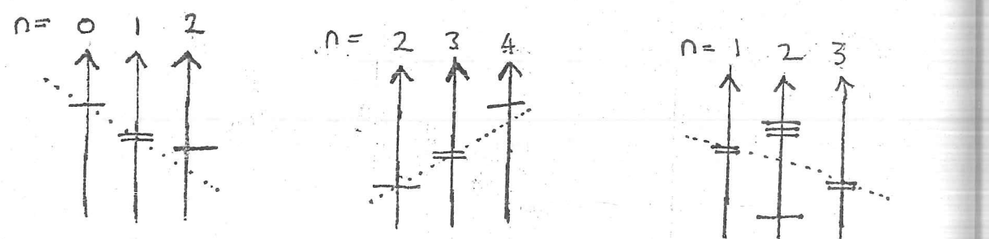
n=2

(a) $\omega = E_d$ (triplet)

(b) $\begin{vmatrix} 2E_d+U-\omega & \sqrt{2}V & 0 \\ \sqrt{2}V & E_d-\omega & \sqrt{2}V \\ 0 & \sqrt{2}V & 0-\omega \end{vmatrix} = 0$

n=4 $\omega = 2E_d+U$

(a) Spectrum of (2.2.10) – general case



(b) $E_d, 2E_d+U \gg V$; $n_d \simeq 0$

$V^{eff}\rho = \frac{-\Delta}{\pi E_d}$

$U^{eff}\rho^2 = \frac{2\Delta^2 U}{\pi^2 E_d^3 (2E_d+U)}$

(c) $-E_d, -(2E_d+U) \gg V$; $n_d \simeq 1$

$V^{eff}\rho = \frac{-\Delta}{\pi(E_d+U)}$

$U^{eff}\rho^2 = \frac{2\Delta^2 U}{\pi^2 (E_d+U)^3 (2E_d+U)}$

(d) $-E_d, E_d+U \gg V$; $n_d \simeq 1$, $S_d \simeq \frac{1}{2}$

$V^{eff}\rho = \frac{\Delta}{2\pi}\left(\frac{1}{E_d}+\frac{1}{E_d+U}\right)$

$J^{eff}\rho = \frac{2\Delta}{\pi}\left(\frac{1}{E_d}-\frac{1}{E_d+U}\right)$

$H^{eff} = V^{eff}\sum_\sigma \psi_\sigma^+\psi_\sigma + U^{eff}\psi_\uparrow^+\psi_\downarrow^+\psi_\downarrow\psi_\uparrow$

$H^{eff} = V^{eff}\sum_\sigma \psi_\sigma^+\psi_\sigma - J^{eff}\vec{S}_d\cdot\frac{1}{2}(\psi^+\vec{\sigma}\psi)$

Fig. (2.2a-d). Spectrum of (2.2.10) (see text).
Note that the ground state is always an n=2 singlet.

be derived by examining the eigenstates of

$$H = E_d \sum_\sigma n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + V \sum_\sigma \psi_\sigma^+ c_\sigma + h.c. \quad (2.2.10)$$

These are shown in Fig. (2.2a). Note that the ground state is always an n=2 singlet.

Examination of the low-lying eigenstates in the three limiting cases (Figs. (2.2b-d)) shows that as far as low energy conduction electrons are concerned, they are characteristic of simple effective Hamiltonians with weak interactions plus potential scattering. In the limits $n_d \simeq 0$ or $n_d \simeq 2$, the effective Hamiltonian is of Wolff form; for $n_d \simeq 1$, there is a spin degree of freedom left in the d-orbital and the effective Hamiltonian is of Kondo form. The effective coupling constants are given by

$$V^{eff}\rho = \frac{-\Delta}{\pi E_d} \quad ; \quad U^{eff}\rho^2 = \frac{2\Delta^2 U}{\pi^2 E_d^3 (2E_d+U)} \quad (n_d \sim 0) \quad (2.2.11)$$

$$V^{eff}\rho = \frac{-\Delta}{\pi(E_d+U)} \quad ; \quad U^{eff}\rho^2 = \frac{2\Delta^2 U}{\pi^2 (E_d+U)^3 (2E_d+U)} \quad (n_d \sim 2) \quad (2.2.12)$$

$$V^{eff}\rho = \frac{\Delta}{2\pi}\left(\frac{1}{E_d}+\frac{1}{E_d+U}\right) \; ; \; J^{eff}\rho = \frac{2\Delta}{\pi}\left(\frac{1}{E_d}-\frac{1}{E_d+U}\right). \quad (n_d \sim 1) \quad (2.2.13)$$

In particular, this last relation between the magnetic regime of the Anderson model and the Kondo model is known as the Schrieffer-Wolff transformation (Schrieffer and Wolff (1966)). Apart from these coupling constants, these effective Hamiltonians also require a bandwidth parameter to characterise their conduction band. Derivation of this is not so straightforward, but it will be of the order of the separation of the next energy level above the low-lying states, as the transformations break down for processes with high energies. Precise evaluation may be achieved by direct comparison of the perturbation expansions in Δ of the Anderson model in each limit with the perturbation expansion for the appropriate effective Hamiltonian. Finally, symmetry properties of the model will be considered. First, a magnetic field term should be added to (2.2.8), coupling to the d-orbital

spin.

$$H' = -H(n_{d\uparrow} - n_{d\downarrow}) \quad . \tag{2.2.14}$$

If the conduction band has particle-hole symmetry (i.e., $\Delta(\omega) = \Delta(-\omega)$), which is the case for the canonical choice $\Delta(\omega)$ constant, the Hamiltonian exhibits various symmetries. Apart from constant terms, the Hamiltonian can be parametrised by (E, H, U), where $E = E_d + \frac{1}{2}U$, and E=0 indicates particle-hole symmetry. The Hamiltonian is unchanged under the following transformations:

(a) $(E,H,U) \rightarrow (-E,H,U)$: (particle-hole (p/h) transformation);

(b) $(E,H,U) \rightarrow (E,-H,U)$: (spin inversion);

(c) $(E,H,U) \rightarrow (H,E,-U)$; (p/h transformation in <u>one</u> spin subspace).

This last is of particular interest, as in zero magnetic field it relates the particle-hole symmetric positive and negative U cases (Iche and Zawadowski (1972)).

This implies that along the boundary separating n=0 from n=2 ground states in Fig. (2.1)the model with finite Δ is equivalent to the Kondo model, with the change that <u>charge</u>, not spin, is fluctuating.

2.3 Properties of the Anderson Model in Mean-Field Theory

The basic character of a system is determined by its energetics, the gross features of which may be obtained by a variational treatment. Hartree-Fock or mean-field theory (MFT) is such a method. Because it is firmly based on a variational theorem, mean-field theory, to the extent that it is valid, is valid at arbitrary interaction strengths.

In perturbation expansions about the non-interacting limit of systems, the approximation of truncating the perturbation series at lowest order is equivalent to MFT for a weakly interacting system. However, MFT is a far more profound approximation than this, because it is not limited to the weak coupling regime, but allows the study of the energetics of strongly coupled systems. In fact, to first order in Δ, mean-field theory and perturbation expansions about the <u>strong</u>-coupling limit of the Anderson model agree, except at the singular lines of configurational instability (Fig. (2.1)) $E_d = 0$, $E_d = -U$, where fluctuations dominate the energetics.

The energetics of a system are largely determined by its high energy fast response modes, which relax almost instantaneously into mean-field-like configurations: where the MFT approximation fails is in the description of the low-energy collective modes that determine the long-timescale behaviour, and the symmetry of the ground state.

MFT often indicates the nature of the missing collective modes by predicting a spuriously broken symmetry. An example is the theory of ellipsoidally deformed nuclei, which are in J = 0 rotation states. Mean-field theory assigns a definite orientation for the nuclear deformation necessary to achieve the lowest energy configuration: the spuriously broken rotational symmetry is accompanied by the

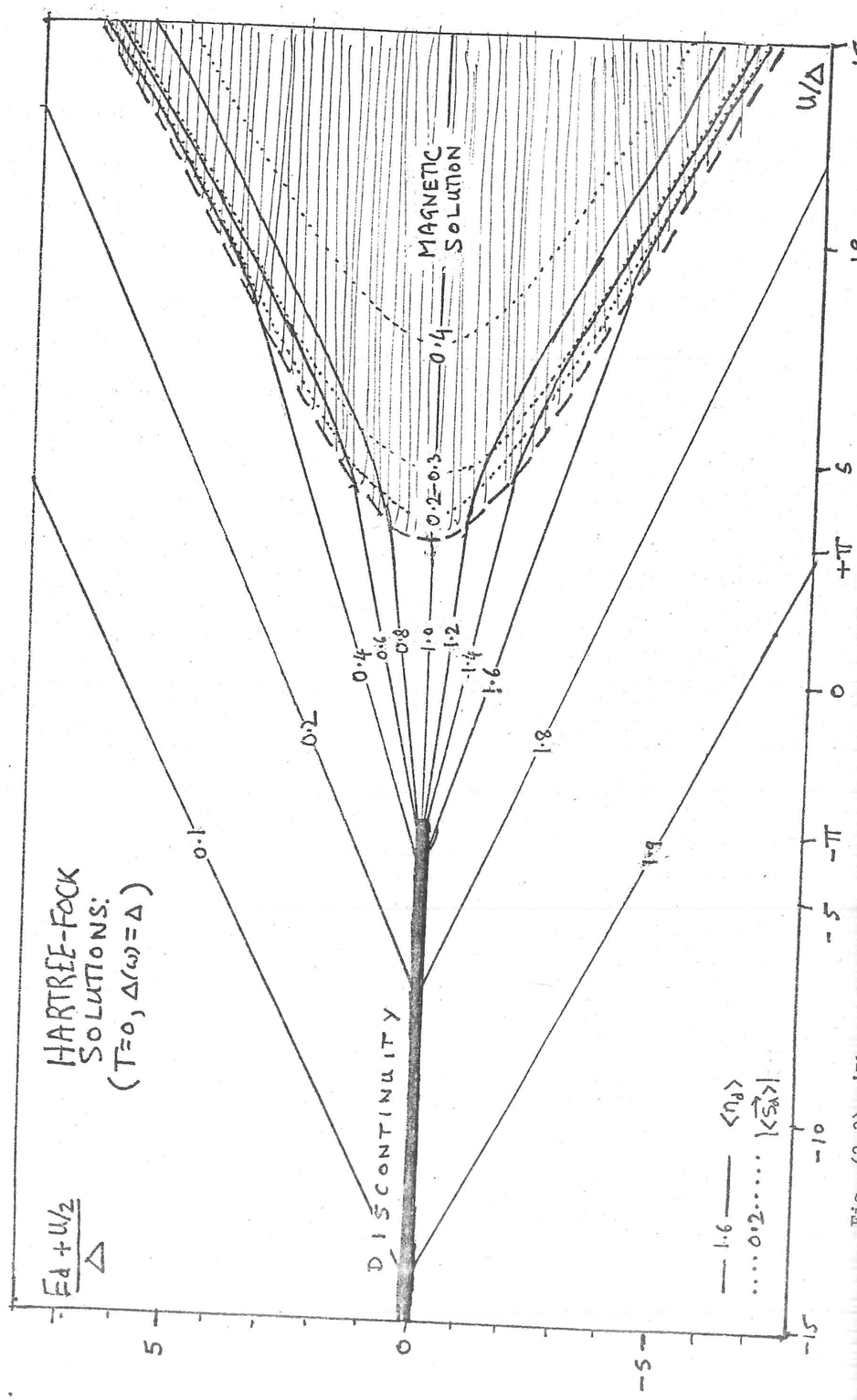


Fig. (2.3). 'Phase diagram' of the Hartree-Fock ground state of the non-degenerate Anderson model.

appearance in random phase approximation (RPA) of a zero energy 'Goldstone' rotational excitation mode. Rotational symmetry may be restored by phenomenologically making the order parameter (the deformation axis) a dynamical variable, leaving its moment of inertia as a phenomenological parameter (to be determined by experiment) that is beyond the scope of MFT or RPA to predict.

Such a modern view of MFT has been recently successfully applied to the thermodynamics of the ferromagnetic transition in nickel, an itinerant ferromagnet (Prange and Korenman (1976)). Local magnetic order must exist both below and above the transition temperature, hence the Stoner criterion governing the occurrence of local moments must be irrelevant in determining the properties of the transition. In the Korenman and Prange treatment, the local band structure corresponds to the magnetic MFT solution, with the magnetisation in some given direction. Long wavelength collective modes, where the order parameter direction varies slowly in space, with little energy cost, must exist. These are controlled by gradient terms which must be inserted into the model 'by hand,' and treated semi-classically. From this ansatz the properties of the transition can be recovered in terms of a few unknown parameters.

The preceding remarks are by way of a tribute to mean-field theory, the virtues of which are often unjustly treated with disdain by 'diagrammaticians' armed with exact theorems about the symmetry of the ground state, which may be violated by MFT. In this work, MFT results, suitably reinterpreted, are used to give a qualitative picture of the true properties of the systems.

The mean-field theory of the Anderson model is a special case of that of the model discussed later, so only the results will be described here.

A 'phase-diagram' of the Hartree-Fock ground state (corresponding to Fig. (2.1) with finite Δ) is given in Fig. (2.3), and values of $\langle n_d \rangle$ and $|\langle \vec{S}_d \rangle|$ are plotted. The horizontal axis is the line of particle-hole symmetry.

By comparison with Fig. (2.1), it is seen that the discontinuity between $\langle n_d \rangle \simeq 0$ and $\langle n_d \rangle \simeq 2$ states has been smoothed out for $|U| < \pi\Delta$ and the magnetic region with non-zero $|\langle \vec{S}_d \rangle|$ is now bounded by a second-order 'phase boundary.' For large negative U the discontinuity between $\langle n_d \rangle \simeq 0$ and $\langle n_d \rangle \simeq 2$ continues to exist. Both the 'phase transitions' and magnetic phase are of course in violation of exact theorems (e.g., Hepp (1970)) stating that for finite Δ, all properties are continuous functions of the model parameters. Deep in the 'magnetic' region, the HF mean spin correctly gives the reduction of the susceptibility in the Curie-law temperature range to first order in Δ.

Various regimes of the expected exact behaviour may be characterised on the basis of the HF diagram (Fig. (2.4)).

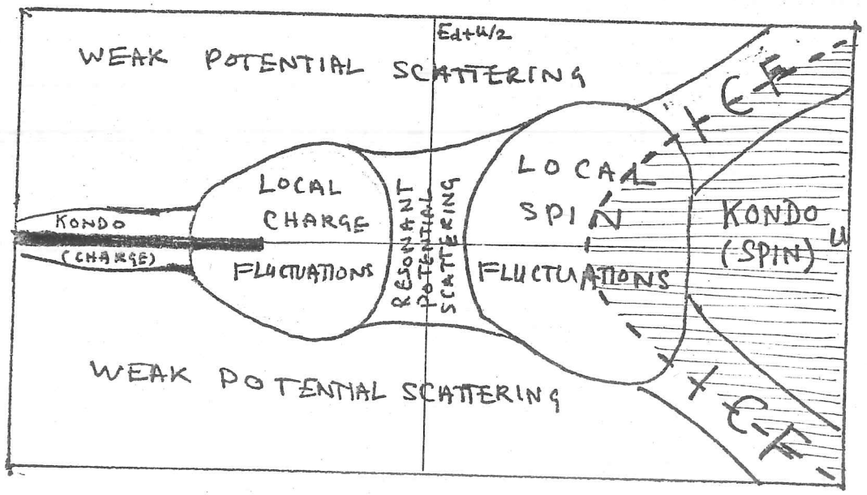


Fig. (2.4). Characterisation of regimes of the Anderson model.

In the weak potential scattering and resonant scattering regions MFT is essentially exact, since interactions may be treated in first order perturbation theory. There are two Kondo regions, the region where $|\langle \vec{S}_d \rangle| \simeq 1/2$, and a corresponding region of Kondo charge fluctuations, where the discontinuity between $\langle n_d \rangle \simeq 0$ and $\langle n_d \rangle \simeq 2$ occurs. By the symmetry relations mentioned at the end of section 2.1, positive and negative U particle/hole symmetric models are isomorphic, so this region of charge fluctuations is equivalent to the region of Kondo spin fluctuations. Since the Kondo fluctuations are very slow collective effects, HF theory is still valid on shorter timescales, as suggested in the earlier discussion.

Also shown in Fig. (2.4) are the crossover regions where the behaviour is intermediate between that in the three main regions. These are regions of strong fluctuations, and HF theory is least adequate there. There are the regions of so-called 'local spin fluctuations' (LSF) (Mills and Lederer (1967)), and the equivalent region of 'local charge fluctuations.' Finally there are the 'interconfigurational fluctuation' (ICF) regions (Hirst (1970)), with valence fluctuations between states with $\langle n_d \rangle \simeq 0$ and 1 or $\langle n_d \rangle \simeq 1$ and 2. These are the regions of interest for the mixed valence problem, and are studied in the later sections of this work.

2.4 The S = ½ Kondo Model

The behaviour of the S = ½ Kondo model (Kondo (1964)), once enigmatic, is now reasonably well understood with the help of modern renormalisation group (RG) techniques. Recalling (2.1.5):

$$H = \sum_{k\sigma} \varepsilon_k c^\dagger_{k\sigma} c_{k\sigma} - J \vec{S} \cdot \tfrac{1}{2} (c_0^\dagger \vec{\sigma} c_0)$$
$$c_{0\sigma} = \sum_k u_k c_{k\sigma} \qquad (2.4.1)$$

(Note that various authors use different conventions for the sign of J, and may omit the factor of ½).

A perturbation expansion in J for the impurity susceptibility yields (Yosida and Okiji (1964))

$$\chi_{imp} = \frac{1}{4T}\left[1 + J\rho + (J\rho)^2 \ln(T/D) + O\left((J\rho)^3 \ln^2(T/D)\right)\right] \qquad (2.4.2)$$

where $\rho = \rho(0)$, and

$$\rho(\omega) = \sum_k |u_k|^2 \delta(\omega - \varepsilon_k) . \qquad (2.4.3)$$

D $(=(D_1 D_2)^{\frac{1}{2}})$ is an effective bandwidth. D_1 and D_2 are particle and hole cutoffs, precisely defined by

$$\ln 2\pi D_1 = C + \lim_{\varepsilon \to 0}\left(\ln\varepsilon + \tfrac{1}{2}\int_\varepsilon^\infty \frac{dx}{x^2}\int_{-x}^{x} dy\, \frac{\rho(\frac{x+y}{2})\rho(\frac{x-y}{2})}{\rho(0)^2}\right) \qquad (2.4.4)$$

C is Euler's constant, 0.57721.... D_2 is given by an analogous expression where $\rho(x) \to \rho(-x)$. Equation (2.4.2) is valid for $T \ll D_1, D_2$ For the usual symmetric case, $D_1 = D_2 = D$, the general n^{th} order term in (2.4.2) has the structure

$$(J\rho)^n \sum_{p=0}^{n-1} \alpha_p \ln^p(T/D) \qquad (2.4.5)$$

Summation of the leading logarithmic terms $(J\rho)^n \ln^{n-1}(T/D)$ (corresponding to the so-called 'parquet' diagrams) leads to (Abrikosov (1965))

$$\chi_{imp} = \frac{1}{4T}\left(1 + \frac{J\rho}{1 - J\rho \ln(T/D)} + \left(\begin{matrix}\text{less divergent}\\ \text{terms}\end{matrix}\right)\right) \qquad (2.4.6)$$

In the antiferromagnetic (AFM) case (Jρ negative), the sum of leading terms grows at lower temperatures, and diverges at a temperature $T^* = D\exp(1/J\rho)$ (formerly identified as the Kondo temperature, T_K); in the ferromagnetic (FM) case, the leading corrections become small, vanishing as $T \to 0$ as $(\ln(T/D))^{-1}$. The structure of the problem became clear following the development of scaling techniques by Anderson and Yuval (Yuval and Anderson (1970), Anderson (1970), Anderson, Yuval and Hamann (1970)), later extended by Armytage (1973). Scaling techniques will be discussed in chapter six; the basic idea is to reduce the bandwidth D by integrating out high energy particle and hole intermediate states during scattering. For small Jρ, it is found that to lowest order, this merely renormalises the matrix element Jρ , scaling one Kondo model to another with different parameters. This scaling property implies 'universality': instead of depending on two parameters D (an energy) and Jρ (dimensionless), the properties of all Kondo models with Jρ small must be the same when expressed in terms of a characteristic energy scale $T_K(J\rho, D)$.

For example:

$$\chi_{imp}(T) = \frac{1}{T_K} f(T/T_K) \qquad (2.4.7)$$

where f(x) is some universal function.

The scaling equation, developed by Anderson, Yuval and Hamann (1970), and extended to second order by Armytage (1973) is

$$\frac{d(J\rho)}{d(\ln D)} = (J\rho)^2 + \tfrac{1}{2}(J\rho)^3 + O(J\rho)^4 \qquad (2.4.8)$$

For Jρ small, this may be integrated:

$$\int d(J\rho)\left(\frac{1}{(J\rho)^2} - \frac{1}{2J\rho} + O(1)\right) = \int d(\ln D) . \qquad (2.4.9)$$

yielding

$$D\exp\left(\frac{1}{J\rho} + \tfrac{1}{2}\ln|J\rho| + O(J\rho)\right) = T_K = \text{constant.} \qquad (2.4.10)$$

The Kondo temperature T_K is an invariant under scaling, and provides the energy scale for 'universal' Kondo behaviour in the weak-coupling AFM case. D may be precisely defined through (2.4.2).

The scaling equations are in fact a systematic method of summing the logarithmic divergences in the perturbation expansion. The

truncation of the series in (2.4.8) after first order yields the quantity T^* as the universal energy scale. The form (2.4.10) was first obtained by Sakurai and Yoshimori (1973) after summing next-most divergent terms in the ground state energy expansion. It is noteworthy that third-most and less divergent terms do not contribute to the non-analytic form of T_K in the $|J\rho| \ll 1$ limit.

The scaling equation (2.4.9) allows immediate solution of the weak coupling FM Kondo problem. As D is reduced $|J\rho|$ gets even smaller, and the correct procedure is to scale to a model with D=T, and a new $\widetilde{J\rho}(T)$

$$\frac{1}{J\rho} + \frac{1}{2}\ln|J\rho| + O(J\rho) = \frac{1}{J\rho} + \frac{1}{2}\ln|J\rho| + O(J\rho) - \ln(T/D) \quad . \quad (2.4.11)$$

For T=D, the logarithmic terms in the perturbation expansion vanish. As $|\widetilde{J\rho}|$ is small, the susceptibility is then given by

$$\chi(T) = \frac{1}{4T}\left(1 + \widetilde{J\rho}(T) + O(\widetilde{J\rho})^2\right) \quad (2.4.12)$$

As $T\to 0$, $\widetilde{J\rho}\to 0$, and $T\chi \to \frac{1}{4}$ for the FM problem. If the scaling equations are truncated at lowest order, the result (2.4.6), the sum of leading divergences, is obtained.

The weak coupling AFM case is not so easily solved. As D is decreased, $|\widetilde{J\rho}|$ increases, and soon it is outside the range of validity of the scaling equation expansion (2.4.8). On heuristic grounds, invoking the fact that in the 'asymptotic' or weak-coupling, low temperature limit there is a correspondence between the partition functio expansion for the Kondo model and that for a certain Ising model (Anderso and Yuval (1971)), Anderson, Yuval and Hamann (1970) argued that the weak coupling AFM Kondo model was equivalent to this Ising model just above its ordering temperature; scaling the Kondo model to larger $|J\rho|$ was equivalent to scaling to Ising models at higher temperatures. The Ising model properties behave smoothly as $T\to\infty$, corresponding to infinite $|J\rho|$ as $D\to 0$. This suggests $|J\rho|\to\infty$, $D\to 0$ is the eventual fixed point of the AFM scaling trajectory, just as $|J\rho|\to 0$, $D\to 0$ was for the

trajectory. At low enough temperatures weak coupling AFM models behave like strong coupling models. The variation of χ with T is schematically shown in Fig. (2.5).

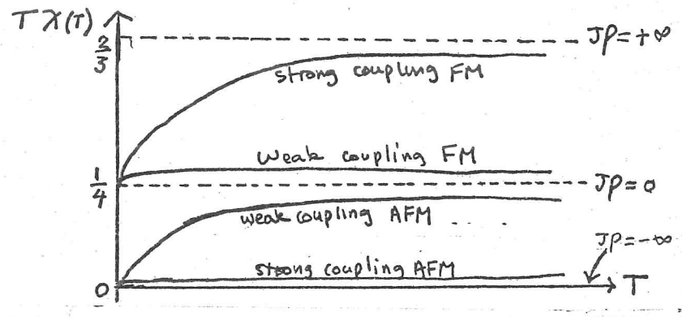


Fig. (2.5)
Temperature dependence of the S=½ Kondo model impurity susceptibility.

It may be remarked that using a procedure similar to that used in section 2.2 to derive the Schrieffer-Wolff transformation, the strong coupling FM S = ½ Kondo model may be transformed to a weak coupling AFM S = 1 model. Similarly, the strong coupling AFM S=1 model is equivalent to the weak coupling FM S = ½ model. The general correspondence (weak, AFM, S) ↔ (strong, FM, S−½), and (weak, FM, S) ↔ (strong, AFM, S+½) may be used to confirm the existence of the $|J\rho|=\infty$ fixed points of the scaling transformations and to determine their stability.

Finally the impressive numerical calculation by Wilson must be mentioned. Wilson (1975) devised an RG scheme that could be carried out numerically on a computer, and succeeded in scaling from the weak coupling AFM model right through to the strong coupling limit, and explicitly calculated the universal function f(x) of (2.4.7).

His method was to study the Hamiltonian:

$$H(\Lambda,N) = -J\vec{S}\cdot\tfrac{1}{2}(c_0^+\vec{\sigma}c_0) + V\sum_{n=0}^{N}\Lambda^{-N/2}\sum_{\sigma}(c_{n+1\sigma}^+ c_{n\sigma} + h.c.) \quad (2.4.13)$$

This describes a tight-binding chain of orbitals coupled to a free spin. In the limit $\Lambda\to 1$, $N\to\infty$, the spectrum projected on the zeroth orbital is continuous, and this is a standard Kondo model with $D\simeq V$. For $\Lambda > 1$, the hopping matrix elements between successive orbitals

decreases as n increases, and the spectrum of $\tilde{e}_0$ becomes discrete, with poles uniformly distributed on a logarithmic scale for positive and negative energies; $\omega = 0$ is a limit point of this sequence of poles (Fig.(2.6)). Since arbitrarily low energy excitations above the Fermi

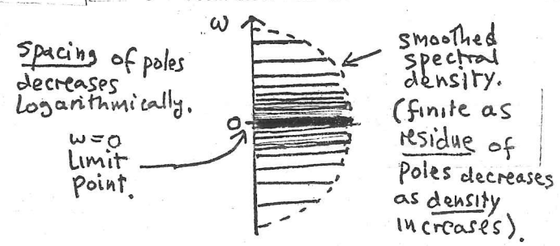


Fig. (2.6)
Spectrum of zeroth orbital in Wilson's Kondo model when $\Lambda > 1$.

level are possible, $\Lambda > 1$ models also show the Kondo effect. If N is finite, the spectrum has a gap of order $D\Lambda^{-\frac{1}{2}N}$ around the Fermi level at $\omega = 0$.

To calculate the properties of the model at temperature T, it is necessary to calculate the low-lying eigenstates of (2.4.13) with finite N so $T \gtrsim D\Lambda^{-\frac{1}{2}N}$.

Wilson calculates the spectrum perturbatively starting from N=0, and adding one orbital at a time to the chain (1.4.12). For $\Lambda \sim 2$ or 3, each new term is a small perturbation on the scale of the previous spectrum. At each stage, Wilson truncates the Hamiltonian, retaining only the lowest 1000 or so eigenstates. For small negative $J\rho$, the succession of small perturbations always eventually causes a drastic modification of the low-energy spectrum to the form characteristic of the case $J\rho \sim -\infty$, confirming Anderson's hypothesis that AFM models always scale to the strong coupling limit. The calculation confirms the form (2.4.10) for T_K. For $T \to 0$, $\chi \simeq 0.103 T_K^{-1}$; at finite temperature the suceptibility of all AFM models maps onto the universal curve (Fig. 2.7)) for $T \ll$ an effective bandwidth parameter $D(J\rho)$; for large $J\rho$, T_K

$\simeq D$, and the 'Kondo effect' disappears, universality being limited to $T \simeq 0$.

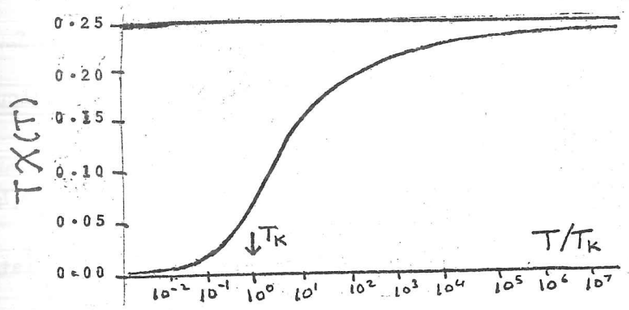


Fig. (2.7).
Universal curve for the temperature-dependent impurity susceptibility of the S=½ AFM Kondo model.
(after Wilson (1975)).

As an aside, it may be pointed out that Wilson's assertion (Wilson (1975)) that the Yuval-Anderson expansion does not reproduce the universal behaviour of the weak coupling Kondo limit is incorrect. He bases this statement on a comparison of his calculation with Schotte's version of the expansion (Schotte (1970)), which does falsify the vital second order term of the scaling equations (2.4.8).* However, the Yuval-Anderson treatment, as demonstrated by Armytage (1973), does give the correct form for T_K.†

Using the fact that the scaling limit is $J\rho \to \infty$, Nozieres (1974) has devised a phenomenological Fermi liquid description of the low temperature properties in terms of a single parameter, which can be fitted to Wilson's result $\chi(0) \simeq 0.1 T_K^{-1}$. Apart from its methodological importance, the achievement of Wilson's calculation is in numerically matching the known high temperature behaviour of the model, and the low temperature behaviour, which is known once the correct scaling limit is identified.

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* A. Luther (private communication) points out that a reworking of Schotte's expansion, retaining the quadratic or 'orthogonality catastrophe' term of the 'X-ray exponent' is sufficient to restore universality.

† Certain additional symmetry arguments outside the long-time approximation are however required.

The Wilson technique may also be used to calculate the exact properties of the Anderson model (Krishna-murthy et al. (1975,1977)). These calculations confirm the Schrieffer-Wolff result

$$J^{eff}\rho = \frac{2\Delta}{\pi}\left(\frac{1}{E_d} - \frac{1}{E_d+U}\right) \qquad (2.4.14)$$

for $|J^{eff}\rho|<0.2$. They are also consistent with the complementary relationship $D_1 \propto -E_d$, $D_2 \propto (E_d + U)$, and hence $D \propto (-E_d(E_d+U))^{1/2}$ (for D_1, D_2 much smaller than any Anderson model bandwidth) first derived in the course of the present work (Section 5.3).

2.5 Derivation of Properties of the Models from Impurity Site Green's Functions

In this section it is shown that all the transport and thermodynamic properties of the class of impurity model being considered may be extracted from a knowledge of the spectrum of a particular single-particle Green's function. The Anderson, Wolff, and Kondo models have the form:

$$H = H^0 + \sum_{\sigma\sigma'} \hat{A}_{\sigma\sigma'} C^+_{o\sigma} C_{o\sigma'} + \hat{B}$$
$$H^0 = \sum_{k\sigma} \varepsilon_{k\sigma} C^+_{k\sigma} C_{k\sigma} \; ; \qquad C_{o\sigma} = \sum_k V_k C_{k\sigma} \qquad (2.5.1)$$

The spin dependence of $\varepsilon_{k\sigma}$ allows for the presence of a magnetic field. $\hat{A}_{\sigma\sigma'}, \hat{B}$ act on some Hilbert space internal to the scatterer. The fundamental single particle Green's function is

$$G_{\sigma\sigma'}(\omega) = \ll C_{o\sigma}; C^+_{o\sigma'} \gg_{\omega,\beta H} \qquad (2.5.2)$$

Where $\ll a;b\gg_{\omega,\beta H}$ is 2π times the conventional Zubarev (1960) double-time thermal Green's function, and satisfies

$$\omega \ll a;b \gg_{\omega,\beta H} = \langle [a,b]_\eta \rangle_{\beta H} + \ll [a,H];b \gg_{\omega,\beta H} \qquad (2.5.3)$$

and has the property:

$$\langle ab \rangle_{\beta H} = \frac{1}{2\pi i} \oint_\Gamma \frac{d\omega}{e^{\beta\omega} - \eta} \ll b;a \gg_{\omega,\beta H} \qquad (2.5.4)$$

Γ is a contour that encloses the real axis: $(-\infty-i\varepsilon) \to (+\infty-i\varepsilon) \to (+\infty+i\varepsilon) \to (-\infty+i\varepsilon) \to (-\infty-i\varepsilon)$; $\eta = \pm 1$ as appropriate for the Fermi/Bose character of a and b. The most general form of the quantity $G_{\sigma\sigma'}(\omega)$ is

$$G_{\sigma\sigma'}(\omega) = g_1(\omega) + g_2(\omega)\, \hat{h}\cdot\vec{\sigma}_{\sigma\sigma'} \qquad (2.5.5)$$

where $\hat{h}$ is direction of any magnetic field (or broken spin symmetry), and $\vec{\sigma}$ are the Pauli matrices. By a suitable choice of spin coordinates

$G_{\sigma,-\sigma}(\omega)$ can be made to vanish. If there is no impurity scattering ($\hat{A}=0$):

$$G_\sigma(\omega) = G^0_\sigma(\omega) \equiv \sum_k \frac{|V_k|^2}{(\omega-\varepsilon_{k\sigma})} \tag{2.5.6}$$

Because of the separable form of the scattering potential, the conduction electron Green's functions must have the form

$$\ll c_{k\sigma}; c^+_{k'\sigma} \gg \equiv G_{kk'\sigma} = \frac{\delta_{kk'}}{(\omega-\varepsilon_{k\sigma})} + (\omega-\varepsilon_{k\sigma})^{-1} \cdot t_{kk'\sigma}(\omega) \cdot (\omega-\varepsilon_{k'\sigma})^{-1} \tag{2.5.7}$$

where the t-matrix has the form $t_{kk'\sigma}(\omega) = v_k t_\sigma(\omega) v^*_{k'}$, and can be constructed from G_σ:

$$G_\sigma = \sum_{kk'} v_k^* G_{kk'\sigma} v_{k'} = G^0_\sigma + G^0_\sigma t_\sigma(\omega) G^0_\sigma \tag{2.5.8}$$

$$t_\sigma = (G_\sigma - G^0_\sigma)/(G^0_\sigma)^2 \quad . \tag{2.5.9}$$

By insertion of (2.5.9) into (2.5.7), it can be verified that $G_{kk\sigma}(\omega)$ no longer has poles at ε_k; they are at the poles of G_σ. If $\hat{B}=0$ (Wolff model, or zero-field Kondo model) the equations of motion may be used to obtain the impurity internal energy $\delta U = \delta\langle H\rangle_{\beta H}$ in terms of G.

$$\sum_{kk'\sigma} (\omega-\varepsilon_{k\sigma}) V_k^* V_{k'} G_{kk'\sigma} = 1 + \sum_{\sigma\sigma'} \ll \hat{A}_{\sigma\sigma'} c_{o\sigma'}; c^+_{o\sigma} \gg \quad , \tag{2.5.10}$$

Using (2.5.7)

$$\sum_{\sigma\sigma'} \ll \hat{A}_{\sigma\sigma'} c_{o\sigma'}; c^+_{o\sigma} \gg = \sum_\sigma G^0_\sigma t_\sigma(\omega) \tag{2.5.11}$$

The conduction electron energy change is obtained from:

$$\sum_{k\sigma} \varepsilon_{k\sigma} \ll c_{k\sigma}; c^+_{k\sigma} \gg = \sum_{k\sigma} \frac{\varepsilon_{k\sigma}}{(\omega-\varepsilon_{k\sigma})} + \frac{\varepsilon_{k\sigma}|V_k|^2}{(\omega-\varepsilon_{k\sigma})} t_\sigma(\omega)$$

$$= \sum_{k\sigma} \varepsilon_{k\sigma} (\omega-\varepsilon_{k\sigma})^{-1} - \sum_\sigma \left(\omega \frac{d G^0_\sigma(\omega)}{d\omega} + G^0_\sigma(\omega)\right) t_\sigma(\omega) \tag{2.5.12}$$

Using (2.5.4), the impurity contribution to the internal energy is just

$$\delta U = -\frac{1}{2\pi i} \sum_\sigma \oint_\Gamma \frac{d\omega}{e^{\beta\omega}+1} \cdot \omega \left(\frac{d}{d\omega} G^0_\sigma(\omega)\right) t_\sigma(\omega) \quad . \tag{2.5.13}$$

G_σ is specified by its spectral density:

$$G_\sigma(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\nu_\sigma(\omega')}{\omega-\omega'} \quad . \tag{2.5.14}$$

From a knowledge of $\nu_\sigma(\omega,T)$, $t_\sigma(\omega)$ and hence $\delta U(T)$ can be constructed. The number of internal states of the impurity gives the entropy δS at $T=\infty$; together with $\delta U(T)$ this allows the free energy $\delta F(T)$ to be constructed, completely specifying all thermodynamic properties.

The transport properties may also be obtained: the quantity of importance is the scattering time $\tau(\omega)$, obtained from the forward scattering amplitudes. Setting $k=k'$ in (2.5.7), and dropping spin indices

$$G_{kk} = \frac{1}{\omega-\varepsilon_k} + \frac{|V_k|^2}{(\omega-\varepsilon_k)^2} t(\omega)$$

$$= (\omega-\varepsilon_k - |V_k|^2 t(\omega))^{-1} + O|V_k|^4 \tag{2.5.15}$$

Since $|V_k|^2 \sim O(1/N)$, the correction term can be neglected in the continuum limit. The inverse scattering time is defined as

$$\tau_k^{-1} = \mathrm{Im}\, t_{kk}(\varepsilon_k - i\delta) \tag{2.5.15}$$

Averaging over all states with energy ω

$$\tau^{-1}(\omega) = \frac{1}{\pi\rho(\omega)} (\nu^0(\omega)\, \mathrm{Im}\, t(\omega)) \tag{2.5.16}$$

where $\rho(\omega)$ is the <u>total</u> density of conduction band states, and $\nu^0(\omega)$ is the spectral density of G^0.

A unitarity bound on the scattering time $(\tau^{-1} < (\pi\rho)^{-1})$ can be obtained by assuming spherical symmetry, in which case (2.5.1) must describe $\ell=0$ scattering only. In the absence of spherical symmetry, the usual derivation becomes invalid. The unitarity bound can, however, be derived on more general grounds, dependent only on the <u>separability</u> of the scattering potential.

Using the separability of the effective scattering potential, $V_{kk'} = V v^*_k v_{k'}$, a Dyson equation for G may be written

$$G(\omega) = G^0 + G^0(\omega) V(\omega) G(\omega) \quad . \tag{2.5.17}$$

Because of the internal structure of the scatterer, $V(\omega)$ is a frequency and temperature dependent effective potential of the form

$$V(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega' \frac{f(\omega')}{\omega-\omega'} + \text{constant.} \qquad (2.5.18)$$

$f(\omega)$ is a real, positive spectral density, with poles at internal excitations of the scatterer. By solving (2.5.17), $t(\omega)$ is easily found in terms of $V(\omega)$:

$$t(\omega) = \frac{V(\omega)}{1-V(\omega)G^0(\omega)} \; . \qquad (2.5.19)$$

Writing $V(\omega-i\epsilon) = V(\omega) + i f(\omega)$, $G^0(\omega-i\epsilon) = R(\omega) + i\pi\rho(\omega)$, for ω real, the scattering time (2.5.10) is given by

$$\tau^{-1}(\omega) = \frac{1}{\pi\rho(\omega)}\left(\frac{(\pi\rho V)^2+(\pi\rho f)^2+(\pi\rho f)}{(1-RV)^2+(\pi\rho V)^2+2(\pi\rho f)+(\pi\rho f)^2+(\pi R)^2}\right) \leq \frac{1}{\pi\rho(\omega)} . \qquad (2.5.20)$$

The inequality (2.5.20) is evident. The condition for maximum scattering, or the unitarity limit, is that $\mathrm{Im}\, V(\omega-i\epsilon)$ and $\mathrm{Re}\,(1-V(\omega)G^0(\omega-i\epsilon))$ are zero.

The properties of the Anderson model are best expressed in terms of the d-orbital Green's function. In particular

$$t(\omega) = V^2 G_d(\omega) . \qquad (2.5.21)$$

where

$$V c_{o\sigma} \equiv \sum_k V_{kd} c_{k\sigma} \; . \qquad (2.5.22)$$

In an analogous fashion to the derivation of (2.5.14), the impurity internal energy is found to be

$$\delta U = \frac{1}{2\pi i}\sum_\sigma \oint_n \frac{d\omega}{e^{\beta\omega}+1}\left[\frac{1}{2}(\omega+E_{d\sigma}) + \left(\frac{1}{2}+\omega\frac{d}{d\omega}\right)\sum_k \frac{|V_{kd}|^2}{(\omega-\epsilon_{k\sigma})}\right] G_{d\sigma}(\omega) \; . \qquad (2.5.23)$$

Mattis (1976) has reported a somewhat similar derivation of thermodynamic properties of these models from a single Green's function. However, his formulae are apparently different from the above, as he seems to have omitted correlation energy terms and identifies 'δU' with only the change in occupation of conduction band states; in particular, his basic equation (his 'Eqn. (6) ') states that the internal energy is given

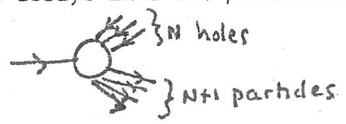
$$"U = \langle H\rangle_H = \frac{1}{\pi}\int_{-\infty}^{\infty} \omega \frac{d\omega}{e^{\beta\omega}+1}\left(\mathrm{Im}\sum_{\delta\to 0^+}\sum_{k\sigma} G_{kk\sigma}(\omega-i\delta)\right) \qquad (2.5.24)$$

The second equality is apparently in error as the correlation terms $\langle \hat{A} c_o^\dagger c_o\rangle$ included here through (2.5.11) have evidently been omitted from $\langle H\rangle_H$; the third quantity in (2.5.24) is just $\langle H\rangle_H o$.

Two key (and much unappreciated) theorems on the zero temperature properties of the Anderson model, due to Langreth (1966) are available. $G_{d\sigma}(\omega)$ may be written as

$$G_{d\sigma}(\omega) = (\omega - E_{d\sigma} - \Sigma_{sd}(\omega) - \Sigma_{dd\sigma}(\omega))^{-1}$$
$$\Sigma_{sd}(\omega) = \sum_k \frac{|V_{kd}|^2}{\omega-\epsilon_k} \equiv \int_{-\nu}^{\nu}\frac{\Delta(x)}{\omega-x}\,dx$$
$$\Sigma_{dd\sigma}(\omega) = \int_{-\nu}^{\infty}\frac{\gamma_\sigma(x)}{\omega-x}\,dx \qquad (2.5.25)$$

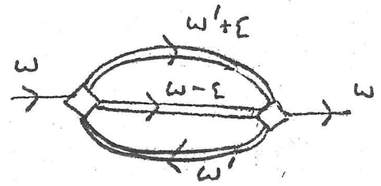
Σ_{sd} is the d-electron self-energy due to hybridisation with the conduction band, present when U = 0; $\Sigma_{dd\sigma}(\omega)$ is the self energy due to interactions between the d-electrons. The amplitude for decay of a particle into more complex excitations is proportional to $\gamma(\omega)$; at low energies, this is sharply limited by the lack of phase space for such decay at the Fermi level. Consider the process where a bare particle decays into N+1 particles and N holes:



For small ω, the density of final states that conserve energy is

$$\rho^N(\omega) \simeq \rho(0)^{2N+1}\int_0^\infty d\omega_1 \cdots d\omega_{2N+1}\,\delta\Big(\omega - \sum_{N=1}^{2N+1}\omega_N\Big)$$
$$\propto (\rho(0))^{2N+1}\frac{\omega^{2N}}{N!} \qquad (2.5.26)$$

where $\rho(0)$ is the fermion density of states at the Fermi level. Thus as $\omega\to 0$ only elastic scattering processes (N=0) are allowed. The dominant contribution to $\gamma(\omega)$ for small ω comes from the N=1 process:



(internal lines and vertices are dressed); thus $\gamma(\omega) \sim O(\omega^2)$ as $\omega \to 0$. Langreth pointed out that the decay time $\tau^{-1}(\omega)$ given by (2.5.16) can be divided into elastic and inelastic contributions:

$$\tau^{-1}_{elastic} = \frac{\Delta(\omega)}{\Delta(\omega)+\gamma(\omega)} \tau^{-1}_{total}$$

$$\tau^{-1}_{inelastic} = \frac{\gamma(\omega)}{\Delta(\omega)+\gamma(\omega)} \tau^{-1}_{total} \qquad (2.5.27)$$

For small enough energies (i.e. at low enough temperatures) elastic processes dominate, and the properties of the model are those of a Fermi liquid.

Elastic scattering may be described by a phase shift; such a description is thus valid for low temperatures and particle energies near the Fermi level. For elastic scattering of electrons in a spherically symmetric conduction band, the t-matrix takes the form:

$$t^{\sigma}_{kk}(\xi_k \pm i\varepsilon) = \frac{1}{\pi\rho(\varepsilon_k)} e^{\pm i\delta^{\sigma}(\varepsilon_k)} \sin\delta_{\sigma}(\varepsilon_k); \qquad (2.5.28)$$

hence, summing over the energy shell:

$$\sum_k t^{\sigma}_{kk}(\xi_k \pm i\varepsilon)\,\delta(\omega-\varepsilon_k) \equiv e^{i\delta_{\sigma}(\omega)} \sin\delta_{\sigma}(\omega) = \Delta(\omega)\, G_{d\sigma}(\omega). \qquad (2.5.30)$$

Since the properties of the model are independent of the individual behaviour of the coefficients v_k, the form (2.5.30) is valid in general, whether or not there is spherical symmetry (recall the similar general validity of the unitarity inequality (2.5.20)). It should once again be emphasised that (2.5.30) is only valid at T=0.

The other theorem pointed out by Langreth (1966) is that the relation between phase shifts at the Fermi surface and impurity charge derived by Friedel (1952) and used in his famous sum rule, and subsequently demenstrated to hold for

interacting systems as well (Langer and Ambegaokar (1961)) also applies to the Anderson model at T=0. Langreth points out the existence of the Ward identity (Luttinger and Ward (1960)) :

$$\lim_{\beta\to\infty} \frac{1}{2\pi i} \oint_{\Gamma} \frac{d\omega}{e^{\beta\omega}+1} \left(\frac{\partial \Sigma_{dd\sigma}(\omega)}{\partial\omega} G_{d\sigma}(\omega) \right) = O(T^2). \qquad (2.5.31)$$

The change in total particle number due to the impurity is

$$\delta\langle n_{\sigma}\rangle = \frac{1}{2\pi i} \oint_{\Gamma} \frac{d\omega}{e^{\beta\omega}+1} \left(\sum_K (G_{KK\sigma} - G^{0}_{KK\sigma}) + G_{d\sigma} \right)$$

$$= \frac{1}{2\pi i} \oint_{\Gamma} \frac{d\omega}{e^{\beta\omega}+1} \left(1 - \frac{\partial \Sigma_{sd}}{\partial\omega}\right) G_{d\sigma} \qquad . \qquad (2.5.32)$$

The addition of (2.5.31) allows this to be integrated directly at T=0:

$$\delta\langle n_{\sigma}\rangle = \frac{1}{2\pi i} \oint \frac{d\omega}{e^{\beta\omega}+1} \left(1 - \frac{\partial \Sigma_{sd}(\omega)}{\partial\omega} - \frac{\partial \Sigma_{dd\sigma}(\omega)}{\partial\omega}\right) G_{d\sigma}(\omega)$$

$$= \frac{1}{2\pi i} \oint \frac{d\omega}{e^{\beta\omega}+1} \left(-\frac{\partial}{\partial\omega} \ln G_{d\sigma}\right)$$

$$= \frac{1}{\pi} \int_{-\infty}^{0} d\omega \; \frac{\partial}{\partial\omega} \arg\left(G_{d\sigma}/\omega - i\varepsilon\right) \qquad (2.5.33)$$

Hence

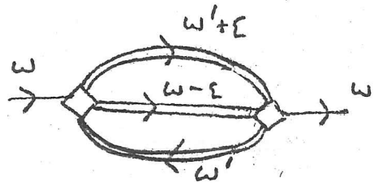
$$\delta\langle n_{\sigma}\rangle = \frac{1}{\pi} \arg G_{d\sigma}(0-i\varepsilon) \quad (T=0) \qquad (2.5.34)$$

Using the form (2.5.30), this is seen to be just the phase shift at the Fermi level. This then gives an <u>exact</u> expression for $G_{d\sigma}(\omega=0)$ in terms of $\delta\langle n_{\sigma}\rangle$ at zero temperature:

$$G_{d\sigma}(0\pm i\varepsilon) = \Delta(0)^{-1} e^{\pm i\delta_{\sigma}} \sin\delta_{\sigma}$$

$$\delta_{\sigma} = \delta\langle n_{\sigma}\rangle \equiv \langle n_{d\sigma}\rangle + \delta\sum_K \langle n_{K\sigma}\rangle \qquad . \qquad (2.5.35)$$

Incidentally, this relation is satisfied by the Hartree-Fock solutions described in section (2.3). The full implications of this relation were not apparent at the time, and require the additional information that, for finite $\Delta(0)$, spin isotropy is never broken in zero magnetic field, and hence $\delta_{\uparrow} = \delta_{\downarrow}$; The consequences of (2.3.35) are discussed in the following section.



(internal lines and vertices are dressed); thus $\gamma(\omega) \sim O(\omega^2)$ as $\omega \to 0$. Langreth pointed out that the decay time $\tau^{-1}(\omega)$ given by (2.5.16) can be divided into elastic and inelastic contributions:

$$\tau^{-1}_{elastic} = \frac{\Delta(\omega)}{\Delta(\omega)+\gamma(\omega)}\ \tau^{-1}_{total}$$

$$\tau^{-1}_{inelastic} = \frac{\gamma(\omega)}{\Delta(\omega)+\gamma(\omega)}\ \tau^{-1}_{total} \qquad (2.5.27)$$

For small enough energies (i.e. at low enough temperatures) elastic processes dominate, and the properties of the model are those of a Fermi liquid.

Elastic scattering may be described by a phase shift; such a description is thus valid for low temperatures and particle energies near the Fermi level. For elastic scattering of electrons in a spherically symmetric conduction band, the t-matrix takes the form:

$$t^{\sigma}_{kk}(\varepsilon_k \pm i\varepsilon) = \frac{1}{\pi\rho(\varepsilon_k)}\, e^{\pm i\delta^{\sigma}(\varepsilon_k)} \sin\delta_{\sigma}(\varepsilon_k); \qquad (2.5.28)$$

hence, summing over the energy shell:

$$\sum_k t^{\sigma}_{kk}(\varepsilon_k \pm i\varepsilon)\,\delta(\omega-\varepsilon_k) \equiv e^{i\delta_{\sigma}(\omega)} \sin\delta_{\sigma}(\omega) = \Delta(\omega)\, G_{d\sigma}(\omega). \qquad (2.5.30)$$

Since the properties of the model are independent of the individual behaviour of the coefficients v_k, the form (2.5.30) is valid in general, whether or not there is spherical symmetry (recall the similar general validity of the unitarity inequality (2.5.20)). It should once again be emphasised that (2.5.30) is only valid at T=0.

The other theorem pointed out by Langreth (1966) is that the relation between phase shifts at the Fermi surface and impurity charge derived by Friedel (1952) and used in his famous sum rule, and subsequently demenstrated to hold for

interacting systems as well (Langer and Ambegaokar (1961)) also applies to the Anderson model at T=0. Langreth points out the existence of the Ward identity (Luttinger and Ward (1960)) :

$$\lim_{\beta\to\infty} \frac{1}{2\pi i}\oint_{\Gamma} \frac{d\omega}{e^{\beta\omega}+1}\left(\frac{\partial\Sigma_{dd\sigma}(\omega)}{\partial\omega}\, G_{d\sigma}(\omega)\right) = O(T^2). \qquad (2.5.31)$$

The change in total particle number due to the impurity is

$$\delta\langle n_{\sigma}\rangle = \frac{1}{2\pi i}\oint_{\Gamma}\frac{d\omega}{e^{\beta\omega}+1}\left(\sum_K (G_{KK\sigma} - G^{0}_{KK\sigma}) + G_{d\sigma}\right)$$

$$= \frac{1}{2\pi i}\oint_{\Gamma}\frac{d\omega}{e^{\beta\omega}+1}\left(1 - \frac{\partial\Sigma_{sd}}{\partial\omega}\right) G_{d\sigma} \qquad . \qquad (2.5.32)$$

The addition of (2.5.31) allows this to be integrated directly at T=0:

$$\delta\langle n_{\sigma}\rangle = \frac{1}{2\pi i}\oint \frac{d\omega}{e^{\beta\omega}+1}\left(1 - \frac{\partial\Sigma_{sd}(\omega)}{\partial\omega} - \frac{\partial\Sigma_{dd\sigma}(\omega)}{\partial\omega}\right) G_{d\sigma}(\omega)$$

$$= \frac{1}{2\pi i}\oint \frac{d\omega}{e^{\beta\omega}+1}\left(-\frac{\partial}{\partial\omega}\ln G_{d\sigma}\right)$$

$$= \frac{1}{\pi}\int_{-\infty}^{0} d\omega\ \frac{\partial}{\partial\omega}\arg(G_{d\sigma}/\omega - i\varepsilon) \qquad (2.5.33)$$

Hence

$$\delta\langle n_{\sigma}\rangle = \frac{1}{\pi}\arg G_{d\sigma}(\omega - i\varepsilon) \quad (T=0) \qquad (2.5.34)$$

Using the form (2.5.30), this is seen to be just the phase shift at the Fermi level. This then gives an <u>exact</u> expression for $G_{d\sigma}(\omega=0)$ in terms of $\delta\langle n_{\sigma}\rangle$ at zero temperature:

$$G_{d\sigma}(0 \pm i\varepsilon) = \Delta(0)^{-1}\, e^{\pm i\delta_{\sigma}} \sin\delta_{\sigma}$$

$$\delta_{\sigma} = \delta\langle n_{\sigma}\rangle \equiv \langle n_{d\sigma}\rangle + \delta\sum_K \langle n_{K\sigma}\rangle \qquad . \qquad (2.5.35)$$

Incidentally, this relation is satisfied by the Hartree-Fock solutions described in section (2.3). The full implications of this relation were not apparent at the time, and require the additional information that, for finite $\Delta(0)$, spin isotropy is never broken in zero magnetic field, and hence $\delta_{\uparrow} = \delta_{\downarrow}$; The consequences of (2.3.35) are discussed in the following section.

2.6 Spectrum of the Impurity Site Green's Function in the Kondo and Anderson Models

Consider the case of a spin exchange-coupled to a free orbital:

$$H = E_0 \sum_\sigma c_{0\sigma}^+ c_{0\sigma} - J\vec{S}\cdot\tfrac{1}{2}(c_0^+ \vec{\sigma} c_0) \qquad (2.6.1)$$

The eigenvalue spectrum of H is shown in Fig. (2.2(d)) on page 22. At zero temperature, for negative J, and $E_0 + 3J/4 > 0$, $E_0 - 3J/4 < 0$, the Green's function $\ll c_{0\sigma}; c_{0\sigma}^\dagger \gg$ has the spectrum (Fig. (2.8)).

$$\mathcal{V}(\omega) = \frac{\pi}{2}\left(\delta(\omega - E_0 + \tfrac{3}{4}J) + \delta(\omega - E_0 - \tfrac{3}{4}J)\right) . \qquad (2.6.2)$$

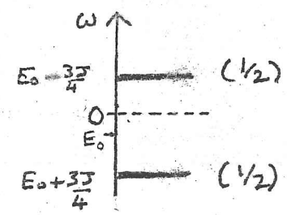


Fig. (2.8)

The spectrum $\mathcal{V}(\omega)$ (see text).

The pole at E_0 has been split into two by the formation of a singlet ground state by exchange-coupling to the spin.

A variational approach to the Kondo model ground state may be taken (Applebaum and Kondo, (1968)), and a trial singlet ground state of the form (2.6.3) chosen:

$$\frac{1}{\sqrt{2}}\left(a_{0\uparrow}^+ \chi_\downarrow - a_{0\downarrow}^+ \chi_\uparrow\right) \prod_{n\neq 1} a_{n\uparrow}^+ a_{n\downarrow}^+ |vac\rangle . \qquad (2.6.3)$$

where $a_0, \{a_k\}$ are linear combinations of $\{c_k\}$, and χ are the spin wavefunctions. The energy is lowest when the singlet state a_0 is made from states c_k with ε_k near the Fermi level. This can be seen in the simpler trial form (2.6.4).:

$$\frac{1}{\sqrt{2}}\left(c_{k\uparrow}^+ \chi_\downarrow - c_{k\downarrow}^+ \chi_\uparrow\right) \prod_{\substack{\varepsilon_{k'}<0 \\ k'\neq k}} c_{k'\uparrow}^+ c_{k'\downarrow}^+ |vac\rangle . \qquad (2.6.4)$$

This has an energy expectation value of

$$\langle H\rangle = |\varepsilon_k| + 3/4\, J \qquad (2.6.5)$$

This is lowest when $|\varepsilon_k|$ is zero, i.e., ε_k right at the Fermi level. Such singlet formation is favoured by antiferromagnetic coupling

(negative J). The absolute value $|\varepsilon_k|$ enters as such a state requires an extra particle to be bound if ε_k is positive, and a hole to be bound if it is negative, thus tying the lowest energy singlet state to the Fermi level.

When the form (2.6.3) is used, the effect that splits the pole of the Green's function in (2.6.2) leads to a hole in the spectral density of G opening up at the Fermi level at low temperatures. The AFM scaling limit $|\tilde{J\rho}(T)| \to \infty$ as $T \to 0$ suggests that the effective scattering potential $V(\omega)$ (2.5.18) develops a pole at $\omega=0$ as $T \to 0$. From (2.5.17)

$$g(\omega) = \frac{g^0(\omega)}{1 - V(\omega) g^0(\omega)} \qquad (2.6.6)$$

So $\mathrm{Im}.G(\omega)\to 0$ as $\omega\to 0$, if $V(\omega)\sim \omega^{-1}$. Likewise (2.5.19) shows that a narrow resonance develops in $t(\omega)$ at the Fermi level. This resonance is known as the Abrikosov-Suhl resonance (Abrikosov (1965), Suhl (1965, 1966)). It is evident in various approximation schemes that attempt to treat scattering self-consistently within Green's function truncation schemes (Nagaoka (1965)), dispersion relation approaches (Suhl (1965, 1966)), and diagram summation (Brenig and Götze (1968)). However, although they qualititatively indicate the formation of such a resonance in $t(\omega)$, these schemes, which turn out to be equivalent (Duke and Silverstein (1967) , Zittartz (1968)), break down in the region of interest.

The width of the resonance will be of order T_K, and $V(\omega) \simeq T_K/(\omega\gamma(0))$. In the case of particle-hole symmetry ($\mathrm{Re}.\, G^0(0) = 0$) $\tilde{\tau}^{-1}(0)$ reaches the unitarity limit; for a non-symmetrical model, (2.5.20) shows that $\tilde{\tau}^{-1}(0)$ reaches $(\pi\rho)^{-1}\sin^2(\arg(G^0(0))$. The likely modification of $\mathrm{Im}.G(\omega)$ for $T < T_K$ is shown in Fig.(2.9).

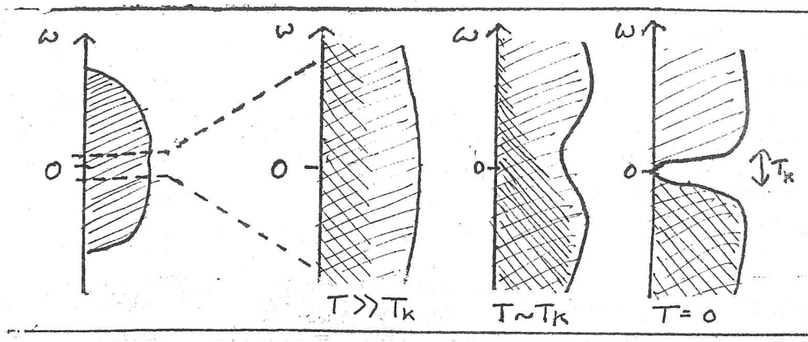


Fig. (2.9) probable modification of Im.G near the Fermi level by the Kondo effect at low temperature

The development of a resonance in the t-matrix corresponds in the Anderson model to the development of a resonance in $G_d(\omega)$ at the Fermi surface since the t-matrix is just $V^2 G_d(\omega)$ (2.5.21). This is particularly seen in studies of the symmetric Anderson model. Because of particle-hole symmetry, Re. $G_d(0) = 0$, and $\delta\langle n_\uparrow\rangle + \delta\langle n_\downarrow\rangle = = 1$. (2.5.35) then reads (at T = 0):

$$\lim_{\omega\to 0} \Delta(\omega)\, G_{d\sigma}(\omega) \;\; = e^{i\delta_\sigma(\omega)} \sin\delta_\sigma(\omega),$$

$$\delta_\uparrow(0) + \delta_\downarrow(0) = \pi \,. \qquad (2.6.7)$$

For finite $\Delta(0)$, there is no magnetisation in zero field, so $\delta\langle n_\uparrow\rangle = \delta\langle n_\downarrow\rangle = \frac{1}{2}$, $\delta_\uparrow(0) = \delta_\downarrow(0) = \frac{1}{2}$, and the scattering cross-section reaches the unitarity limit. Im.$G_d(0)$ is thus $\Delta(0)^{-1}$. (For $\Delta(0) = 0$, the alternative <u>magnetic</u> solution is $\delta_\uparrow = \pi$, $\delta\langle n_\uparrow\rangle = 1$, $\delta_\downarrow = 0$, $\delta\langle n_\downarrow\rangle = 0$). Thus <u>independent of the value of U</u>, Im $G_d(0)$ is fixed at $\Delta(0)^{-1}$ for finite $\Delta(0)$. The impurity linear specific heat may be evaluated using (2.5.23); noting that by symmetry $\frac{d}{d\omega}$Im.$G_d(\omega=0) = 0$:

$$\frac{\delta C}{C} = \frac{1}{\pi\rho(0)}\left(\frac{1}{\Delta(0)}\left(1 - \frac{d}{d\omega}\mathrm{Re}\Sigma_{sd}(0)\right) + \Delta(0)\frac{d}{d\omega}\mathrm{Re}\, G_d(0)\right) \qquad (2.6.8)$$

From (2.6.7), (2.5.25)

$$\Delta(0)\frac{d}{d\omega}\mathrm{Re}\,G_d(\omega=0) = \frac{d}{d\omega}\delta(\omega=0)$$

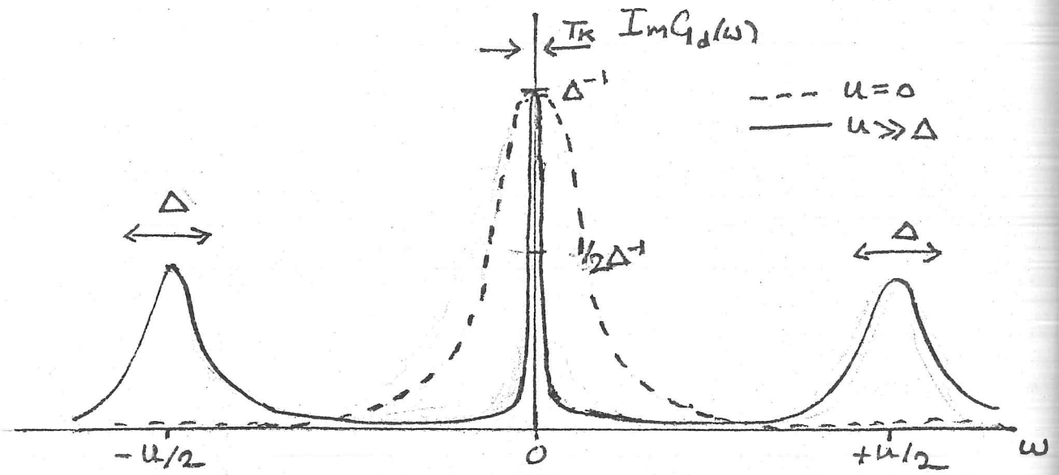
$$= \frac{1}{\Delta(0)}\left(1 - \frac{d}{d\omega}\mathrm{Re}\left(\Sigma_{dd}+\Sigma_{sd}\right)\right)_{\omega=0} \qquad (2.6.9)$$

If the phase shift when U=0 is denoted by $\delta^0(\omega)$, the impurity specific heat may be written

$$\frac{\delta C}{C} = \frac{1}{\pi\rho}\left(2\left(\frac{d\,\delta^0(\omega)}{d\omega}\right)_{\omega=0} + \left(\frac{d\left(\delta(\omega)-\delta^0(\omega)\right)}{d\omega}\right)_{\omega=0}\right). \qquad (2.6.10)$$

For U = 0, and specialising to the case $\Delta(\omega) = \Delta$, constant, Im.$G_d(\omega) = \Delta/(\omega^2+\Delta^2)$, and $\frac{d}{d\omega}\delta^0(\omega) = \Delta^{-1}$. For large U, in zero magnetic field, (2.5.23) shows that the energy is determined solely by $\sum_\sigma G_{d\sigma}(\omega)$; <u>since it satisfies a variational principle, the Hartree-Fock value of this quantity cannot differ greatly from the true value except at small energies.</u> The true solution is of course non-magnetic, so the true Greens function must be close to the Hartree-Fock one, averaged over spin. The Hartree-Fock solution becomes exact in the limit $U\to\infty$. For large U, the HF solutions show that the main weight of Im.$G_d(\omega)$ is divided between resonances of width Δ and height $\frac{1}{2}\Delta^{-1}$ at $= \pm\frac{1}{2}U$; however since Im.$G_d(\omega=0) = \Delta^{-1}$ for all U at T = 0, a very narrow resonance whose width is the Kondo temperature T_K must be left at the Fermi surface, containing the very small fraction T_K/Δ of the total weight (Fig.2.10). Since Re.G_d is the Hilbert transform of Im.G_d, $\Delta(0)\frac{d}{d\omega}$Re.$G_d(\omega=0)$ $\left(= \frac{d}{d\omega}\delta(\omega)\Big|_{\omega=0}\right)$ is of order $1/T_K$. For large U, this is the dominant contribution to the specific heat (2.6.10).

The passage to the $U/\Delta\to\infty$ limit is singular in that the <u>height</u> of the Fermi surface resonance stays constant, but its <u>width</u> vanishes. This singularity will be seen in chapter five to give rise to divergencies in perturbation expansions in Δ for finite U at T = 0.



(Fig. 2.10). $Im.G_d(\omega)$ at T = 0 for the symmetric, constant Δ Anderson model with U = 0 (broken curve) and $U \gg \Delta$ (solid curve). Note the resonance at the Fermi surface which is always present at T=0 in addition to the Hartree-Fock resonances at $\pm \frac{1}{2}U$.

This behaviour is confirmed in detail by Yamada's (1975) perturbation calculation in U, which shows a large degree of cancellation of diagrams in each order, and hence has good convergence properties well beyond the limit $U = \pi\Delta$ where the Hartree-Fock and Random Phase Approximations diverge. His Fig.(3.5) shows $Im.G_d(\omega)$ at T=0 for a series of increasing values of U. For $U/\pi\Delta = 5$, the limiting large U behaviour of a narrow resonance at the Fermi surface, superimposed on Hartree-Fock resonances at $\pm \frac{1}{2}U$, is well established.

At $T > T_K$, inelastic scattering at the Fermi surface becomes important, and the sum rules that require the Fermi surface resonance no longer hold; the resonance thus disappears, and a rotationally symmetrised Hartree-Fock picture becomes essentially exact.

Similar considerations can be applied to the asymmetric case. Specialising to the case Δ= constant, where there is no conduction electron polarisation, (2.3.35) implies

$$Im\, G_d(0) = \Delta^{-1} \sin^2 \frac{\pi}{2}\langle n_d \rangle \qquad (2.6.11)$$

$$Re\, G_d(0) = \frac{1}{\pi} P \int_{-\nu}^{\nu} \frac{Im G_d(\omega')}{\omega - \omega'} d\omega'$$

$$= \Delta^{-1} \cos\pi \frac{\langle n_d \rangle}{2} \sin\pi \frac{\langle n_d \rangle}{2} \qquad (2.6.12)$$

where $\langle n_d \rangle$ is the total d-orbital occupancy, summed over spin. (2.6.11) clearly shows that whenever the Hartree-Fock solution is magnetic, with one resonance well below the Fermi level and another well above, so that $\langle n_d \rangle \simeq 1$, a narrow resonance of height Δ^{-1} and width $T_K \ll \Delta$ must be present at the Fermi level at T = 0. For such a case, a sequence of plots of $Im.G_d(\omega)$ for decreasing temperatures is shown in Fig.(2.11).

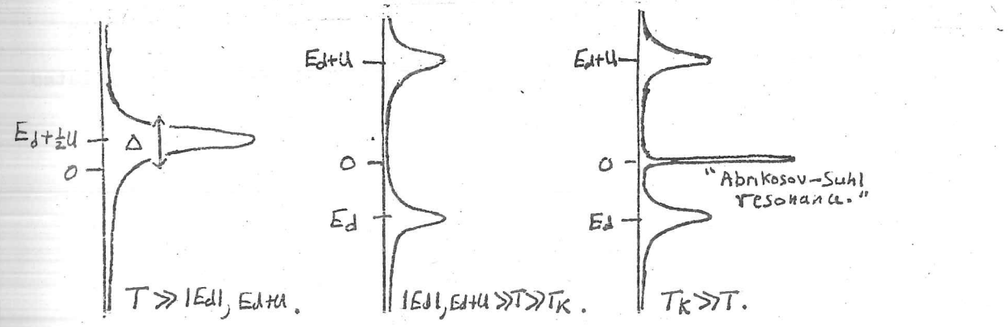


Fig. (2.11); Temperature dependence of $Im.G_d(\omega)$; $(E_d << 0 << E_d+U)$.

At high temperatures, there is no magnetic HF solution, and there is a single resonance in the spectrum. At lower temperatures the resonance splits into two as the local moment develops. Mean-field theory is least reliable at this intermediate temperature, where strong 'local spin fluctuations' will occur. At lower temperatures, HF theory is reliable, until the onset of the Kondo regime, where the Abrikosov-Suhl resonance develops at the Fermi level.

A sequence of T=0 Hartree-Fock solutions as E_d rises is shown in fig. (2.12). They illustrate the transition from magnetic ($\langle n_d \rangle \simeq 1$) states to non-magnetic ($\langle n_d \rangle \simeq 0$) states. In these two limits the HF results are

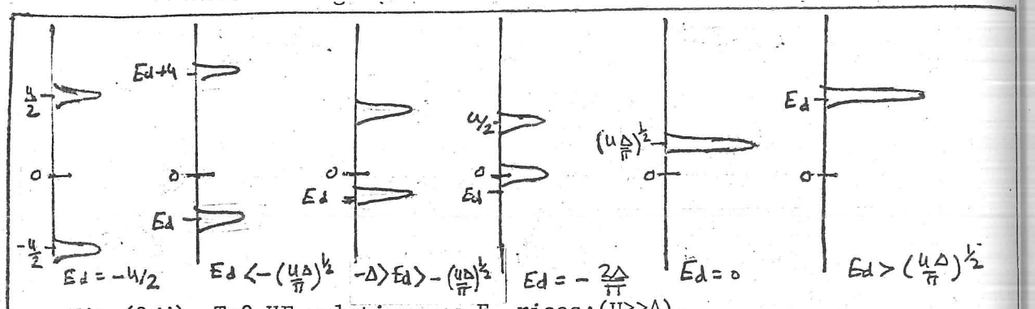


Fig (2.11). T=0 HF solutions as E_d rises; (U>>Δ).

reliable (after superposition of the Fermi level resonance in the magnetic case) because the energy associated with the residual fluctuations omitted in HF theory is small compared to the HF energy. However, the solutions in the crossover regime where $\langle n_d \rangle$ differs substantially from 0 or 1 are quite unreliable, as fluctuations are strong, and have associated energies of the same order as the HF energy.

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CHAPTER THREE

GENERALIZATION OF THE ANDERSON MODEL TO INCLUDE DYNAMIC SCREENING PROCESSES

3.1 Physical Incompleteness of the Anderson Model in the Valence Fluctuation Regime

The Anderson model was originally devised for the study of the formation and properties of local magnetic moments; these are now fairly well understood, and interest has shifted to its properties in the valence fluctuation regime; this is a natural choice of a model for investigating 'mixed valence' effects. The model parameters are chosen so it is in a condition of configurational instability: $E_d \simeq 0$, (n_d=0,1) or $E_d \simeq -U$, (n_d=1,2). On inclusion of the hybridisation term, the configurations are strongly mixed. Recently Krishna-murthy et al. (1977) have applied the Wilson renormalisation group technique to this problem; the results of these studies will be mentioned later.

Although this model may seem to be the 'natural' one to use in this context, it is in fact physically incomplete in one very fundamental way: it does not allow the Friedel sum rule to be satisfied. In these impurity models, the charged electrons have been renormalised to non-interacting quasi-particles by the Fermi liquid scheme; this imposes the constraint of local charge neutrality on possible effective impurity potentials. This is expressed as the Friedel sum rule, which in this context takes the form:

$$\frac{1}{2\pi i}\oint_\Gamma e^{\beta\omega}+1 \; \frac{d\omega}{} \; \mathrm{Tr}_k \left(G_{kk}(\omega) - G^0_{kk}(\omega)\right) + \langle n_d \rangle = n_0 \qquad (3.1.1)$$

$\langle n_d \rangle$ is the electronic charge associated with the impurity; n_0 is the nominal ionic charge. (3.1.1) states that the charge density of the conduction electrons must respond to exactly screen out any impurity charge, within some finite region, so there are no infinite range effects produced by the impurity.

In cases where the configuration of the impurity is static, the

Friedel sum rule (3.1.1) is satisfied by regarding the Anderson model parameter E_d as an effective parameter chosen so the impurity charge is neutralised. This was done in the initial study of the (orbitally degenerate) Anderson model to understand the systematics of local moment occurrence across the transition metal series (Clogston et al. (1962)). Such an ad hoc approach to the charge neutrality constraint is perfectly adequate in configurationally stable models where all charge fluctuation processes are virtual. If there is a local moment, spin fluctuation processes will dominate the dynamics, and departures from charge neutrality only occur as transients during a 'spin-flip' process. In the case of configurational instability, however, such arguments fail. Such a situation entails the existence of a two different quasi-stable configurations, representing different charge states of the impurity orbital, both of which must satisfy the charge neutrality requirement. With only one parameter to vary, such simultaneous obedience of (3.1.1) is impossible. This can be seen in detail as follows: using a phase-shift formulation appropriate for general (i.e., not necessarily spherical) point symmetry, the Friedel sum rule takes the form:

$$\langle n_d \rangle + \frac{1}{\pi}\delta_{\Gamma_0}(0) + \frac{1}{\pi}\sum_{\Gamma \neq \Gamma_0} d_\Gamma \, \delta_\Gamma(0) = n_0 \qquad (3.1.2)$$

$\delta_\Gamma(0)$ is the 'phase shift' of conduction band states belonging to point group representation Γ (with multiplicity d_Γ) at the Fermi level. The impurity orbital belongs to representation Γ_0; $d_{\Gamma_0}=1$ in the non-degenerate case. Only conduction band states with that symmetry will interact with the impurity orbital by hybridisation; all other $\delta_\Gamma(\omega)$ will be zero. (In the 'flat' density of states model, $\Delta(\omega)$ constant, $\delta_{\Gamma_0}(\omega)$ is also zero, and $\langle n_d \rangle$ is the only term in (3.1.2) dependent on the model parameters.) The quantity $\langle n_d \rangle + \pi^{-1}\delta_{\Gamma_0}(\omega)$ is a monotonically

decreasing function of the parameter E_d, so there is only one value of E_d that solves (3.1.2). If there are to be two solutions to (3.1.2), at least one other phase shift $\delta_{\Gamma'}(\omega)$ must be able to vary, so that

$$\langle n_d \rangle + \pi^{-1}(\delta_{\Gamma_0} + d_\Gamma \delta_\Gamma) = \langle n_d \rangle' + \pi^{-1}(\delta_{\Gamma_0}' + d_\Gamma \delta_\Gamma') \quad (3.1.3)$$

this implies that an explicit screening mechanism involving scattering by the impurity in channels other than those with Γ_0 symmetry must be included. Such a model is proposed in the next section.

3.2 Rederivation of the Anderson Model to Include Screening Processes

The physical situation under consideration is that of a rare-earth impurity in a transition metal (or rather a rare-earth material from which the f-orbitals on all sites but one have been omitted, as a prelude to studying the full problem). The conduction band may be thought of as a tight binding d-band with one set of d-orbitals per site. It can be represented either by Bloch states, or reorganised into representations of the point group symmetry of the impurity site:

$$H^c = \sum_{\vec{k}n\sigma} \varepsilon_{\vec{k}n} C^+_{\vec{k}n\sigma} C_{\vec{k}n\sigma} \equiv \sum_{\Gamma\mu i\sigma} \varepsilon_{\Gamma i} C^+_{\Gamma\mu i\sigma} C_{\Gamma\mu i\sigma} \quad . \quad (3.2.1)$$

n=1..5 is a band index: since there are five d-orbitals per site, there are five bands. Γ labels irreducible representations with multiplicity d_Γ ; $\mu=1,..,d_\Gamma$ indexes the components of each representation. If H^c is written in a basis reflecting the lower point symmetry, the disguised translational invariance of H^c gives rise to 'accidental' degeneracy, which is broken by the introduction of an impurity. This is reflected by the 'accidental' proportionality of the density of states of each representation:

$$\sum_i \delta(\omega - \varepsilon_{\Gamma i}) = \frac{d_\Gamma}{p} \sum_{\vec{k}n} \delta(\omega - \varepsilon_{\vec{k}n}) \quad (3.2.2)$$

p $(=\sum_\Gamma d_\Gamma^2)$ is the order of the point group. The usual Anderson model description of the impurity orbital can now be used. At this point a notational difficulty is encountered. In this context the impurity orbital physically represents an f-orbital, though conventionally in the Anderson model it is labelled '$c_{d\sigma}$'. This would cause confusion with the impurity-site Wannier orbital, which <u>is</u> a d-orbital. In this section the labels 'f' and 'd' will be used to represent the <u>physical</u> interpretation of the orbitals. When the model has been derived, the

notation will revert to the conventional form '$c_{d\sigma}$' for the impurity orbital.

The f-orbitals are described by

$$H^{imp} = E_f \sum_{m\sigma} c^+_{fm\sigma} c_{fm\sigma} + U \sum_{m\sigma \neq m'\sigma'} n_{fm\sigma} n_{fm'\sigma'} \quad (+ \text{exchange}) \qquad (3.2.3)$$

It will be convenient to make the usual simplification by specialising to a non-degenerate 'f' orbital, and dropping the m-labels in (3.2.3). If the f-orbital belongs to the (singlet) representation Γ_0 of the point group, the hybridisation term is

$$H^{hyb} = \sum_i V_i c^+_{\Gamma_0 i\sigma} c_{f\sigma} + h.c. \quad ; \qquad (3.2.4)$$

to generalise the Anderson model, screening terms must be included. The most important intra-atomic term not included so far is the Coulomb interaction between the d- and f-orbitals of the impurity.

$$H^{scr.} = g \sum_\sigma n_{f\sigma} \sum_{m\sigma'} n_{dm\sigma'} \; . \qquad (3.2.5)$$

Such a term gives rise to a screening mechanism sufficient to satisfy the charge neutrality condition.

The configurational instability that will be investigated is really of the type

$$f^{n+1} d^m + e^-(\ell=2) \rightleftharpoons f^n d^{m+1} + e^-(\ell=3) \qquad (3.2.6)$$

This reaction satisfies charge neutrality, but needs the substrate conduction band to 'catalyse' it as the wave function of the free electro associated with it must change symmetry. In the free atom (or at least in the simple model of one considered here), this is a symmetry-forbidden internal transition. The d-orbitals are also the impurity site Wannier functions, and they will be assumed to belong to representations other than Γ_0, reflecting the symmetry prohibition of the direct transition $f^{n+1} d^m \not\rightarrow f^n d^{m+1}$. The Hamiltonian can then be written in two parts, $H = H^{And} + H^{scr}$:

$$H^{And} = \sum_{i\sigma} \varepsilon_i c^+_{\Gamma_0 i\sigma} c_{\Gamma_0 i\sigma} + E_f \sum_\sigma n_{f\sigma} + U n_{f\uparrow} n_{f\downarrow} + \sum_i V_i c^+_{\Gamma_0 i\sigma} c_{f\sigma} + h.c \qquad (3.2.7)$$

$$H^{scr} = \sum_{\substack{\Gamma\neq\Gamma_0 \\ \mu i\sigma}} \varepsilon_{\Gamma i} c^+_{\Gamma\mu i\sigma} c_{\Gamma\mu i\sigma} + g \sum_\sigma n_{f\sigma} \sum_{\substack{\Gamma\neq\Gamma_0 \\ \mu i j\sigma}} V^\Gamma_{ij} c^+_{\Gamma\mu i\sigma} c_{\Gamma\mu j\sigma} \; . \qquad (3.2.8)$$

H^{And} is just the standard Anderson model; the new feature is the screening term H^{scr}, where

$$c_{dm\sigma} = \sum_{\Gamma\mu i} \upsilon_{\Gamma\mu i m} c_{\Gamma\mu i\sigma} \qquad (3.2.9)$$

$$V^\Gamma_{ij} = \sum_m \upsilon^*_{\Gamma\mu i m} \upsilon_{\Gamma\mu j m} \qquad (3.2.10)$$

Note that V^Γ_{ii} is necessarily positive. Because $c_{dm\sigma}$ are the impurity site Wannier functions, the density of states projected onto these orbitals is proportional to the conduction band density of states $\sigma(\omega)$

$$\sum_{\Gamma\mu i m} |\upsilon_{\Gamma\mu i m}|^2 \delta(\omega - \varepsilon_{\Gamma i}) = \sum_{\Gamma\mu i\sigma} V^\Gamma_{ii} \delta(\omega - \varepsilon_\Gamma) = \tfrac{1}{N} \sigma(\omega). \qquad (3.2.11)$$

The effective screening parameter g is <u>not</u> a free parameter of the theory, but must be chosen so as to satisfy the Friedel sum rule. In this respect it may be said to have been renormalised from its 'bare' value by the Fermi liquid scheme. In the limit $V_i = 0$, n_f is a good quantum number, and the charge neutrality condition (3.1.1) becomes, in Born approximation

$$g \langle n_f \rangle \cdot \frac{Im}{2\pi i} \oint_n \frac{d\omega}{e^{\beta\omega}+1} \sum_{\Gamma\mu i} \frac{V^\Gamma_{ii}}{(\omega - \varepsilon^\Gamma_i)} + \langle n_f \rangle = 0 \qquad (3.2.12)$$

Using (3.2.11)

$$\left[1 - \frac{g}{N} \int_{-\infty}^{\infty} d\omega\, \sigma(\omega) \frac{d}{d\omega}\left(\frac{-1}{e^{\beta\omega}+1}\right)\right] \langle n_f \rangle = 0 \qquad (3.2.13)$$

this fixes g so that

$$g \sum_{\Gamma\mu i} V^\Gamma_{ii} \delta(\omega - \varepsilon_i) = \sigma(\omega) \Big/ \left[\int_{-\infty}^{\infty} d\omega\, \sigma(\omega) \left(\frac{-1}{e^{\beta\omega}+1}\right)'\right] \simeq \frac{\sigma(\omega)}{\sigma(0)} \qquad (3.2.14)$$

The screening condition thus reads

$$g \sum_{\Gamma\mu i\sigma} V^\Gamma_{ii} \delta(0 - \varepsilon_i) \simeq 1 \qquad (3.2.15)$$

In Born (linear) approximation, the impurity is now screened whether $\langle n_f \rangle = 0$,

1, or 2. Born approximation is good in the limit of a very degenerate conduction band; there are essentially $d=2x(2\ell+1)=10$ scattering channels involved in the screening response. When d is large, each channel need only respond slightly, so its phase shift $\simeq\pi/d$ when the impurity charge state charges by 1. For small phase shifts, the response will be effectively linear.

When the response is linear, another useful simplification is possible. The $\Gamma\neq\Gamma_0$ electrons of H^{scr} respond passively to fluctuations in n_f with density fluctuations. When these are small enough to be linear, the resemblance of the charge density excitation spectrum to a boson spectrum may be exploited to rewrite H^{scr} in a formally simpler, if physically more obscure, boson form (Section 3.4).

At this point, the notation for the model reverts to the usual form, with '$c_{d\sigma}$' labelling the impurity orbital:

$$H^{And.}=\sum_{k\sigma}\varepsilon_k c^\dagger_{k\sigma}c_{k\sigma}+E_d\sum_\sigma n_{d\sigma}+U n_{d\uparrow}n_{d\downarrow}+\sum_{k\sigma}V_{kd}c^\dagger_{k\sigma}c_{d\sigma}+h.c. \qquad (3.2.1)$$

$$H^{scr}=\sum_{k\alpha}E_{k\alpha}a^\dagger_{k\alpha}a_{k\alpha}+g\sum_\sigma n_{d\sigma}\sum_{kk'\alpha}V^\alpha_{kk'}a^\dagger_{k\alpha}a_{k'\alpha} \qquad (3.2.1)$$

where

$$g\sum_{k\alpha}V^\alpha_{kk}\delta(\omega-E_{k\alpha})=\frac{\sigma(\omega)}{\sigma(0)}\;;\quad gV^\alpha_{kk}>0\,. \qquad (3.2.1)$$

In H^{scr}, the screening electrons have been represented as $a_{k\alpha}$ to emphasize that they are distinct from the electrons taking part in hybridisation, and their various conserved spin and symmetry indices have been contracted into a single index α .

3.3 The Tomonaga Boson Representation

In this section, the Tomonaga boson representation (Tomonaga (1950)) usually used in the study of the one-dimensional interacting Fermi gas, is rederived in a form suitable for impurity problems, and shown to be equivalent to a linear approximation. The usual formulation is in terms of momentum variables, and requires a restrictive form of band structure, which is necessary for the 1-D electron gas but irrelevant for the impurity problem, where only energy variables need be used.

In some arbitrary basis, consider the following fermion scattering problem (which may be time dependent) where H^0 has a continuous single-particle spectrum at the Fermi level:

$$H^0=\sum_i\varepsilon_i c_i^\dagger c_i$$
$$H=H^0+\lambda(t)\sum_{ij}v_{ij}c_i^\dagger c_j \qquad (3.3.1)$$

A 'charge fluctuation operator,' $\rho(E)$ may be defined.

$$\rho(E)=\sum_{ij}v_{ij}\delta(\varepsilon_i-\varepsilon_j+E)\left(c_i^\dagger c_j-\langle c_i^\dagger c_j\rangle_{H^0}\right)\,. \qquad (3.3.2)$$

$\rho(E)$ has the property

$$\int_{-\infty}^{\infty}dE\,\rho(E)=\sum_{ij}v_{ij}\left(c_i^\dagger c_j-\langle c_i^\dagger c_j\rangle_{H^0}\right)\,. \qquad (3.3.2)$$

It satisfies $\rho^\dagger(E)=\rho(-E)$, and

$$[\rho(E),H^0]=E\rho(E) \qquad (3.3.4)$$

$\rho(E)$ has complicated commutation relations:

$$[\rho(E),\rho(E')]=\sum_{ijk}\left(\delta(\varepsilon_i-\varepsilon_k+E)\delta(\varepsilon_k-\varepsilon_j+E')-\delta(\varepsilon_i-\varepsilon_k+E')\delta(\varepsilon_k-\varepsilon_j+E)\right)v_{ik}v_{kj}\,c_i^\dagger c_j\,. \qquad (3.3.5)$$

Nevertheless, they are on the whole 'boson-like' in character, as may be seen by taking the expectation value of the commutator in the system H^0.

$$\langle [\rho(E), \rho(E')] \rangle_{H^0} = \delta(E+E') \sum_{ij} |v_{ij}|^2 \delta(\varepsilon_i - \varepsilon_j + E)(\langle n_i \rangle_{H^0} - \langle n_j \rangle_{H^0}) . \quad (3.3.6)$$

By normalising ρ, we can define the boson-like operator $b(E)$

$$b(E) = \rho(E) / (f(E))^{1/2} \qquad (E > 0) .$$

$$\langle [b(E), b^+(E')] \rangle_{H^0} = \delta(E-E') \; ; \; \langle [b(E), b(E')] \rangle_{H^0} = 0 \quad (3.3.7)$$

By comparison with (3.3.6) $f(E)$ is linear in E as $E \to 0$:

$$f(E) = \sum_{ij} |v_{ij}|^2 \delta(\varepsilon_i - \varepsilon_j + E)(\langle n_i \rangle_{H^0} - \langle n_j \rangle_{H^0}) , \quad (3.3.8)$$

$$\lim_{E \to 0} \frac{f(E)}{E} = \int_{-\nu}^{\nu} d\omega \, \frac{d}{d\omega}\left(\frac{-1}{e^{\beta\omega}+1}\right) \cdot \sum_{ij} |v_{ij}|^2 \delta(\omega - \varepsilon_i)\delta(\omega - \varepsilon_j) . \quad (3.3.9)$$

Since it is Hermitian, v_{ij} may be written as

$$v_{ij} = \sum_{\lambda}' V_\lambda v_{i\lambda}^* v_{j\lambda} \qquad (V_\lambda \text{ real}) \quad (3.3.10)$$

For low temperature, (3.3.9) becomes

$$\lim_{E \to 0} \frac{f(E)}{E} = \sum_{\lambda\lambda'}' V_\lambda V_{\lambda'} \left| \sum_i v_{i\lambda}^* v_{i\lambda'} \delta(0 - \varepsilon_i) \right|^2 . \quad (3.3.11)$$

It may be noted that in Born approximation, the change in the number of occupied states (when $\lambda(t)=1$) is given by:

$$\int_{-\infty}^{\infty} d\omega \cdot \left(\frac{-1}{e^{\beta\omega}+1}\right)' \cdot \left| \sum_i v_{ii} \delta(\omega - \varepsilon_i) \xrightarrow{(T \to 0)} \sum_\lambda V_\lambda \left(\sum_i |v_{i\lambda}|^2 \delta(0 - \varepsilon_i) \right) \right| . \quad (3.3.12)$$

Only in the special case where each λ corresponds to a different value of ℓ, m (or a different representation of the point symmetry group) can (3.3.11) be represented as a sum of squares of 'phase shifts' defined via (3.3.12) (as in the Schotte and Schotte (1969) treatment of the X-ray problem).

The spirit of the Tomonaga approximation is to treat the mean commutation relations (3.3.7) as exact, and regard the $b(E)$ as true bosons. The Hamiltonian becomes :

$$H = \langle H \rangle_{H^0} + \int_0^\infty dE \cdot E b^\dagger(E) b(E) + \lambda(t) (f(E))^{1/2} \left(b(E) + b^\dagger(E) \right) . \quad (3.3.13)$$

or, in less cumbersome notation,

$$H = \langle H \rangle_{H^0} + \sum_i \omega_i b_i^\dagger b_i + \lambda(t) \sum_i (\alpha_i b_i + h.c)$$

$$[b_i, b_j^\dagger] = \delta_{ij} \text{ etc} \; ; \; \sum_i |\alpha_i|^2 \delta(\omega - \omega_i) = f(\omega) . \quad (3.3.14)$$

A diagrammatic interpretation is available (Fig. 3.1) ; the linked cluster expansion shows that the Tomonaga approximation

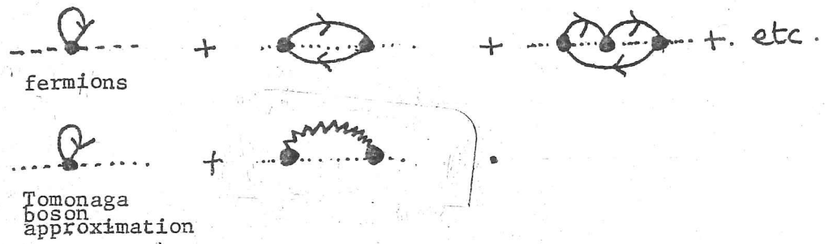

Fig. (3.1) (see text).

reproduces perturbation theory to second order. It is thus valid for small coupling constant <u>provided perturbation theory is convergent</u>.

The Tomonaga representation is useful as it reproduces the infra-red divergences or 'orthogonality catastrophe' associated with the response of a Fermi gas to a time-dependent potential. Suppose $\lambda(t) = \lambda\theta(t)$. The ground state of

$$H_\lambda = \sum_i \omega_i b_i^\dagger b_i + \lambda \sum_i \alpha_i b_i + h.c \quad (3.3.15)$$

is

$$|\lambda\rangle = \exp -\left(\frac{\lambda^2}{2} \sum_i \frac{|\alpha_i|^2}{\omega_i^2}\right) \exp -\sum_i \frac{\alpha_i}{\omega_i} b_i^\dagger \; |0\rangle \quad (3.3.16)$$

The overlap between two such coherent states is given by

$$\langle \lambda | 0 \rangle = \exp -\frac{\lambda^2}{2} \sum_i \frac{|\alpha_i|^2}{\omega_i^2} = \exp -\frac{\lambda^2}{2} \int_0^\infty dE \; \frac{f(E)}{E^2} \quad (3.3.17)$$

As $f(E) \sim E$ as $E \to 0$, the integral is divergent, and the overlap vanishes for any finite λ . The ground state of H_λ is thus unobtainable by perturbation theory. This reflects the fact that, given long enough, <u>any</u> finite potential will excite infinitely many particle-hole excitations, which can be made with arbitrarily low energy if there is a free Fermi surface. However, the perturbation expansion for the ground

state energy is convergent, as the divergent number of particle-hole excitations carry infinitesimal energy.

If $f(E) \sim \varepsilon E$ as $E \to 0$, the amplitude for the system still to be in the ground state of H^0 a time t after the potential has been switched on is

$$\langle 0|e^{iH^0t}e^{-iH_\lambda t}|0\rangle = \exp\left[+i\left(\lambda^2\sum_i \frac{|\alpha_i|^2}{\omega_i}\right)t\right]\exp\left[-\lambda^2\sum_i\frac{|\alpha_i|^2}{\omega_i^2}\left(1-e^{-i\omega_i t}\right)\right]$$
$$\simeq \exp[i\Delta E(\lambda)t]\cdot\left[\frac{t}{t_0(\lambda)}\right]^{-\varepsilon(\lambda)} \quad (t\to\infty). \tag{3.3.18}$$

ΔE is the (finite) ground state energy shift; t_0 is a characteristic response time of the system. The exponent ε characterises the relaxation of the system about the scattering potential. This behaviour can also be seen directly in the fermion representation. In fact, ε will be given by a power series expansion in λ: $\varepsilon = a\lambda^2 + b\lambda^3 \ldots$, where the Tomonaga approximation stops at the lowest order term.* The Tomonaga method, because it allows the direct construction of the various ground states, leads to a particularly clear demonstration of the infra-red anomalies of the Hamiltonian (3.3.1).

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* Similarly:

$$\Delta E(\lambda) = a'\lambda^2 + b'\lambda^3 \ldots .$$
$$t_0(\lambda) = t_0 + b''\lambda \ldots .$$

3.4 Boson Representation of Screening Processes

The screening term H^{scr} (3.2.17) is analogous to the model treated in the last section, as it describes a Fermi gas that reacts to a time-dependent scattering potential, in this case due to the quantum fluctuations of $n_{d\sigma}$. Since H^{scr} is itself just an ansatz valid in linear approximation, it is convenient to replace it by the equivalent boson representation, which is easier to handle. The screening terms become

$$H^{scr} = \left(g\sum_{k\alpha} V^{\alpha}_{kk}\langle a^+_{k\alpha}a_{k\alpha}\rangle_{H^0}\right)\sum_\sigma n_{d\sigma} + \sum_q \omega_q b^+_q b_q + g\sum_\sigma n_{d\sigma}\sum_q \alpha_q b_q + \text{h.c.} \tag{3.4.1}$$

where

$$f(\omega) \equiv g^2\sum_q |\alpha_q|^2\delta(\omega-\omega_q) = g^2\sum_{kk'\alpha}|V^q_{kk'}|^2\delta(E_{k\alpha}-E_{k'\alpha}+\omega)\left(\langle n_{k\alpha}\rangle_{H^0}-\langle n_{k'\alpha}\rangle_{H^0}\right). \tag{3.4.2}$$

The first term can be absorbed into the impurity energy level, E_d .

From the origin of $V^\alpha_{kk'}$ as screening by the impurity-site Wannier orbital, (3.2.10)

$$V^\alpha_{kk'} = \sum_m U^{*\alpha}_{km}U^\alpha_{k'm} \quad . \tag{3.4.3}$$

The characteristic exponent ε, is given by

$$\lim_{\omega\to 0}\frac{f(\omega)}{\omega} \equiv \varepsilon \simeq \sum_\alpha\left(\sum_{km}|U^\alpha_{km}|^2\delta(0-E_{k\alpha})\right)^2 \quad . \tag{3.4.4}$$

The screening condition is, from (3.2.15):

$$\sum_\alpha\left(\sum_{km}|U^\alpha_{km}|^2\delta(0-E_{k\alpha})\right) = 1 \quad . \tag{3.4.5}$$

Since there are d (=10) Wannier orbitals labelled by m,σ , the exponent ε which reflects the Friedel sum rule, obeys the inequality:*

$$\frac{1}{d} \leq \varepsilon < 1 \quad . \tag{3.4.6}$$

The lower bound is the case where all d orbitals participate equally

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* In the absence of a magnetic field, spin degeneracy requires $\varepsilon < 1/2$.

in the screening process. Crystal field terms, which split the d-levels, will raise ε somewhat above this lower limit. The boson spectral density $f(\omega)$ remains roughly linear in ω up to $\omega \sim D$, the bandwidth of the conduction band. It is mainly characterised by the behaviour it gives rise to in the long-time or 'asymptotic' limit (discussed later). This is described by the ground state energy shift due to the boson relaxation after a change in $n_{d\sigma}$; given by

$$C = \int_0^\infty d\omega \, \frac{f(\omega)}{\omega} \sim \frac{D}{d} \tag{3.4.7}$$

and the singular behaviour as $\omega \to 0$, characterised by ε and $\tau \sim D^{-1}$, where

$$\lim_{x \to 0} \int_0^\infty d\omega \, \frac{f(\omega)}{\omega^2} (1 - e^{-\omega x}) = -\varepsilon \ln(x/\tau) \, . \tag{3.4.8}$$

Valence changes in the very localised f-orbitals of a rare-earth atom cause relatively large charges in the ionic radii, with the result that configurational fluctuations will be strongly coupled to local distortions of the lattice around the impurity site. Such phonon coupling may be notionally included in the boson screening term. The contributions to $f(\omega)$ are shown in Fig. (3.2).

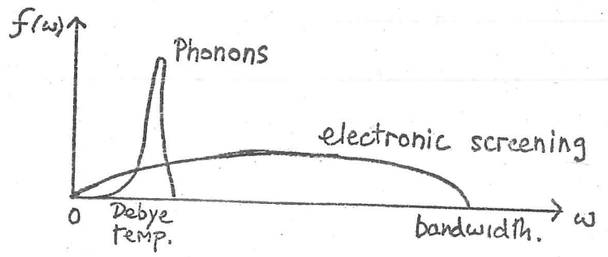

Fig. (3.2). Relative contributions to $f(\omega)$ from phonon and electronic screening processes.

The phonons do not change the infra-red exponent ε, but will increase C somewhat, and, as the overlap between coherent phonon states relaxed about different configurations of the impurity may be small (Sherrington and Von Molnar(1975)) may greatly decrease τ. ε, τ, and C should thus be regarded as essentially independent parameters.

3.5 Other Uses of the Tomonaga Model

The Tomonaga transformation as applied above to screening in the Anderson model is a well-defined small coupling constant approximation. The same procedure could be applied to the Kondo model, resulting in a model of a spin coupled to a vector boson field; in this case the procedure is not valid as perturbation theory in the Kondo model coupling constant is divergent, so truncation of the expansion after the second order term falsifies the behaviour of the model. Other formulations of the Tomonaga model have been applied to the X-ray and Kondo models (Schotte and Schotte (1969), Schotte (1970)). These treatments reproduce the long-time behaviour of the relevant propagators, but often encounter scepticism, as they involve the use of an operator 'identity,' which is only 'asymptotically' exact, to express single fermion operators in terms of bosons. Because of the somewhat dubious reputation of these procedures, it should be emphasized that they are not involved in the use of the Tomonaga representation in this work.

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CHAPTER FOUR

MEAN-FIELD THEORY OF THE ANDERSON MODEL COUPLED TO A SLOW BOSON FIELD.

4.1 The Mean Field Theory and Variational Function.

The Anderson model with coupling to bosons will now be studied in its own right. The effect of the boson modes will depend on whether their response is faster or slower than the characteristic electronic fluctuation time Δ^{-1}. If the bosons are phonons the dominant modes have frequencies of order ω_D, the Debye frequency (see, for example, Fig. (3.2)); two different types of behaviour will be found according to whether Δ is greater or less than ω_D.

For $\Delta \ll \omega_D$, the (fast) phonons respond adiabatically to the electronic charge fluctuations, renormalising the electronic parameters in a way discussed in section 5.5. For $\omega_D \ll \Delta$ the mean field approximation, where the bosons see only the average electronic distribution, is appropriate. The next level of approximation beyond this is the Born-Oppenheimer approximation, where the boson field can move around its mean position in an effective potential derived from the adiabatic reponse of the electrons to the instantaneous dispacement of the boson field.

The case of Tomonaga bosons, derived in section 3.4 as a representation of the electronic screening response modes, is more complicated. Since the spectral density is linear from a high energy cutoff of the order of the conduction bandwidth right down to $\omega = 0$, both high and low frequency modes are present. After renormalisation of the electronic parameters by the high frequency modes, the remaining low frequency modes (i.e., those slower than the renormalised characteristic electronic frequency) must be treated by the mean field approximation of this chapter. Further discussion of this separation of the Tomonaga boson spectrum into fast and slow components is postponed until a later chapter, and a treatment of the Anderson model with coupling to slow boson modes is now presented.

A finite temperature version of Hartree-Fock theory may be based on the free-energy inequality

$$F(H) \leq F(H^{eff}) + \langle H - H^{eff} \rangle_{H^{eff}}. \qquad (4.1.1)$$

This is the generalisation of the Rayleigh-Ritz inequality, and holds for any partition of H into H^{eff} and $(H-H^{eff})$. If H^{eff} is a free-particle Hamiltonian, Wick's theorem can be used to disentangle correlation terms in $\langle H-H^{eff} \rangle_{H^{eff}}$. The mean field equations are generated by finding the free-particle Hamiltonian H^{eff} that minimises the RHS of (4.1.1). If

$$H = \sum_{ij} H_{ij} c_i^\dagger c_j + \tfrac{1}{2} \sum_{ijkl} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l \qquad (4.1.2)$$

and

$$H^{eff} = \sum_{ij} h_{ij} c_i^\dagger c_j \qquad (4.1.3)$$

The quantity to be minimised is

$$F(H^{eff}) + \sum_{ij} H_{ij} - h_{ij} \langle c_i^\dagger c_j \rangle_{H^{eff}} + \tfrac{1}{2} \sum_{ijkl} V_{ijkl} \left(\langle c_i^\dagger c_l \rangle_{H^{eff}} \langle c_j^\dagger c_k \rangle_{H^{eff}} - \langle c_i^\dagger c_k \rangle_{H^{eff}} \langle c_j^\dagger c_l \rangle_{H^{eff}} \right). \qquad (4.1.4)$$

varying h_{ij} leads to the Hartree-Fock effective Hamiltonian

$$h_{ij} = H_{ij} + \sum_{kl} \left(V_{iklj} - V_{iklj} \right) \langle c_k^\dagger c_l \rangle_{H^{eff}} . \qquad (4.1.5)$$

h_{ij} may be restricted to the form (4.1.5) with $\langle c_k^\dagger c_l \rangle$ (no subscript) replacing the expectation value $\langle c_k^\dagger c_l \rangle_{H^{eff}}$ in (4.1.5) as a parameter to be determined variationally. The HF equation then reads

$$\langle c_k^\dagger c_l \rangle = \langle c_k^\dagger c_l \rangle_{H^{eff}} . \qquad (4.1.6)$$

The Hamiltonian under consideration is

$$H = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_q \omega_q b_q^\dagger b_q + E_d \sum_\sigma c_{d\sigma}^\dagger c_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + g \sum_\sigma n_{d\sigma} \sum_q \alpha_q b_q + h.c + \sum_{k\sigma} V_{kd} c_{k\sigma}^\dagger c_{d\sigma} + h.c. \qquad (4.1.7)$$

The variational parameters needed are $\langle b_q \rangle$, $\langle b_q^\dagger \rangle$, and the four quantitites $\langle c_{d\sigma}^\dagger c_{d\sigma'} \rangle$, which can be regrouped into $\langle N_d \rangle = \tfrac{1}{2} \delta_{\sigma\sigma'} \langle c_{d\sigma}^\dagger c_{d\sigma'} \rangle$ and $\langle \vec{S}_d \rangle = \tfrac{1}{2} \vec{\sigma}_{\sigma\sigma'} \langle c_{d\sigma}^\dagger c_{d\sigma'} \rangle$.

The spin axis for the effective Hamiltonian may be chosen so it is aligned with $\langle \vec{S}_d \rangle$, so that $\langle c_{d\uparrow}^\dagger c_{d\downarrow} \rangle$ vanishes.

Writing

$$b_q' = b_q - \langle b_q \rangle \qquad (4.1.8)$$

$$E_\sigma^{eff} = E_d + U \langle n_{d-\sigma} \rangle + g \sum_q \alpha_q \langle b_q \rangle + h.c. \qquad (4.1.9)$$

the effective Hamiltonian can be constructed:

$$H^{eff} = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_\sigma E_\sigma^{eff} n_{d\sigma} + \sum_{k\sigma} V_{kd} c_{k\sigma}^\dagger c_{d\sigma} + h.c + \sum_q \omega_q b_q^{\dagger\prime} b_q' + \sum_q \left[\omega_q \langle b_q^\dagger \rangle + g \alpha_q^* \sum_\sigma \langle n_{d\sigma} \rangle \right] b_q' + h.c \qquad (4.1.10)$$

$$H - H^{eff} = -\left[U \langle n_{d\uparrow} \rangle \langle n_{d\downarrow} \rangle + \sum_q \omega_q \langle b_q^\dagger \rangle \langle b_q \rangle + g \sum_\sigma \langle n_{d\sigma} \rangle \sum_q \alpha_q^* \langle b_q^\dagger \rangle + h.c \right] + U \left(n_{d\uparrow} - \langle n_{d\uparrow} \rangle \right) \left(n_{d\downarrow} - \langle n_{d\downarrow} \rangle \right) + g \sum_\sigma \left(n_{d\sigma} - \langle n_{d\sigma} \rangle \right) \sum_q \alpha_q b_q' + h.s. \qquad (4.1.11)$$

It is easily shown that the variational equation for $\langle b_q \rangle$ is only satisfied if the linear boson term in (4.1.10) vanishes, so that

$$\langle b_q \rangle = -g \sum_\sigma \langle n_{d\sigma} \rangle \cdot \alpha_q^* / \omega_q \qquad (4.1.12)$$

The displacement of the boson field gives rise to an effective attractive interaction between electrons with coupling constant C.

$$C = 2g^2 \sum_q \frac{|\alpha_q|^2}{\omega_q} \qquad (4.1.13)$$

The effective Hamiltonian reduces to

$$H^{eff} = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_\sigma E_\sigma^{eff} n_{d\sigma} + \sum_{k\sigma} V_{kd} c_{k\sigma}^\dagger c_{d\sigma} + h.c \qquad (4.1.14)$$

$$E_\sigma^{eff} = E_d - C \langle n_{d\sigma} \rangle + (U - C) \langle n_{d-\sigma} \rangle \qquad (4.1.15)$$

This effective Hamiltonian shows an important new feature due to the bosons; in addition to responding to the average occupation number of d-electrons of opposite spin, the d-electron responds to its <u>own</u> average occupation number. This comes about because the Pauli principle effect that prevents two electrons from being in the same state and hence usually prevents such electrons interacting only rules out <u>instantaneous</u> interactions: $n_{d\sigma}(t) n_{d\sigma}(t')$ is in general <u>not</u> equal to $n_{d\sigma}(t)$ unless $t = t'$. The slow bosons introduce a highly retarded interaction by which a d-electron can

interact with electrons of the same spin in the same orbital at earlier times. In plainer language, an electron may cause displacements of the slow boson field which remain long after it has moved away, and may in the future act to attract it back to its past position, effectively allowing the electron to "interact with itself". This phenomenon is well known in polaron theory, where, if the electron phonon coupling is strong enough, the electron may "dig" itself a potential well so deep that it becomes bound, greatly enhancing its effective mass, since it cannot move without dragging its well along with it. A feature related to such "self-trapping" will be seen in the mean field analysis of the model under consideration here.

The free energy $F(H^{eff})$ is easily evaluated in closed form (see appendix to this chapter) using Green's function equation of motion techniques and coupling constant integration. The variational function becomes:

$$F(H^{eff}) + \langle H - H^{eff}\rangle_{Heff} = F^{\circ}(E') - \frac{1}{2\pi i}\oint_{\Gamma} \frac{d\omega}{e^{\beta\omega}+1}\left[\sum_{\sigma} \ln\left(\frac{\omega - E_{\sigma}^{eff} - \Sigma(\omega)}{\omega - E'}\right)\right] - U\langle n_{d\uparrow}\rangle\langle n_{d\downarrow}\rangle + \tfrac{1}{2}C\left(\sum_{\sigma}\langle n_{d\sigma}\rangle\right)^2 \tag{4.1.16}$$

where

$$\Sigma(\omega) = \sum_{k} \frac{|V_{kd}|^2}{\omega - \varepsilon_k} \quad ; \tag{4.1.17}$$

$$F^{\circ}(E') = F\left(\sum_{k\sigma}\varepsilon_k n_{k\sigma} + \sum_{q}\omega_q b_q^{\dagger} b_q + E'\sum_{\sigma} n_{d\sigma}\right) . \tag{4.1.18}$$

E' is arbitrary.

It is convenient to define the function

$$n(x) = \frac{1}{2\pi i}\oint_{\Gamma} \frac{d\omega}{e^{\beta\omega}+1}\left(\omega - x - \Sigma(\omega)\right)^{-1} \tag{4.1.19}$$

The expectation value $\langle n_{d\sigma}\rangle_{Heff}$ is given by

$$\langle n_{d\sigma}\rangle_{Heff} = n(E_{\sigma}^{eff}) \tag{4.1.20}$$

$n(x)$ decreases monotonically from 1 to 0 as x increases. This can be seen from the spectral form

$$(\omega - x - \Sigma(\omega))^{-1} = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega' \frac{\nu(x,\omega')}{\omega - \omega'} \tag{4.1.21}$$

where $\nu(x,\omega)$ is real, positive, and normalised to π. Then:

$$n(x) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{d\omega}{e^{\beta\omega}+1}\,\nu(\omega,x) \quad ; \tag{4.1.22}$$

hence $0 \le n(x) \le 1$ with equality only at $\pm\infty$ (except in the singular case $\beta=\infty$, $\Sigma(\omega)=0$). Taking the derivative of (4.1.21) with respect to x :

$$\begin{aligned} n'(x) &= \frac{1}{2\pi i}\oint_{\Gamma} \frac{d\omega}{e^{\beta\omega}+1}\,\frac{1}{(\omega - x - \Sigma(\omega))^2} \\ &= \frac{1}{\pi^2}\int_{-\infty}^{\infty} du\,\nu(u,x)\int_{-\infty}^{\infty} dv\,\nu(v,x)\cdot\frac{1}{2\pi i}\oint_{\Gamma}\frac{d\omega}{e^{\beta\omega}+1}\,\frac{1}{(\omega-u)(\omega-v)} \\ &= \frac{1}{\pi^2}\int_{-\infty}^{\infty} du\,\nu(u,x)\int_{-\infty}^{\infty} dv\,\nu(v,x)\cdot\frac{1}{u-v}\left(\frac{1}{e^{\beta u}+1} - \frac{1}{e^{\beta v}+1}\right) \le 0 \end{aligned} \tag{4.1.23}$$

The variational functional (4.1.16) may be rewritten in terms of E_{σ}^{eff} as the variational parameters by using (4.1.15) to eliminate $\langle n_{d\sigma}\rangle$ in favour of E_{σ}^{eff}. Writing $x = E_{\uparrow}^{eff}$, $y = E_{\downarrow}^{eff}$;

$$\begin{aligned} F(H^{eff}) + \langle H - H^{eff}\rangle_{Heff} &= F(x,y) \\ &+ \frac{C}{2(U-2C)^2}\left[2E_d + (U-2C)\left(n(x)+n(y)\right) - (x+y)\right]^2 \end{aligned} \tag{4.1.24}$$

where the function $F(x,y)$ is:

$$\begin{aligned} F(x,y) = \text{const.} &+ E_d\left(n(x)+n(y)\right) + U n(x) n(y) - \tfrac{1}{2}C\left(n(x)+n(y)\right)^2 \\ &- \int_{0}^{x} dz\, z n'(z) - \int_{0}^{y} dz\, z n'(z) . \end{aligned} \tag{4.1.25}$$

$F(x,y)$ is a smooth function of x and y and bounded below ($F(x,y) > -2|E_d| - |U| - 2C +$ const., at worst). It thus has an absolute minimum at a solution of:

$$\frac{\partial F}{\partial x} = n'(x)\left(E_d - C\,n(x) - (U-C)\,n(y) - x\right) = 0 \; ; \; \frac{\partial F}{\partial y} = 0 . \tag{4.1.26}$$

Since $n'(x) < 0$, the Hartree-Fock equations must be satisfied at such a minimum:

$$x = E_d - C\,n(x) + (U-C)\,n(y) \; ; \; y = E_d - C\,n(y) + (U-C)\,n(x) . \tag{4.1.27}$$

Thus, at a minimum, the non-negative second term in the variational function (4.1.24) vanishes, with the result that:

$$F(H^{eff}) + \langle H - H^{eff}\rangle_{Heff} \ge F(x,y) \ge F(H) \tag{4.1.28}$$

$F(x,y)$, a function with stationary points only at solutions of the Hartree-Fock equations (4.1.24), may thus be used to obtain a variational approximation to the true free energy. It may be objected that the Hartree-Fock equations can be obtained far more directly, and that the cumbersome procedure to arrive at (4.1.28) is unnecessary. However, it will turn out that there are multiple stable solutions of these Hartree-Fock equations, and a variational functional is indispensable to determine which solution is globally minimum.

Finally, it may be remarked that when magnetic solutions with $x \neq y$ are found, these have $\langle \vec{S}_d \rangle$ along the z-axis. By a spin rotation such solutions are of course degenerate with those where $\langle \vec{S}_d \rangle$ is in an arbitrary direction.

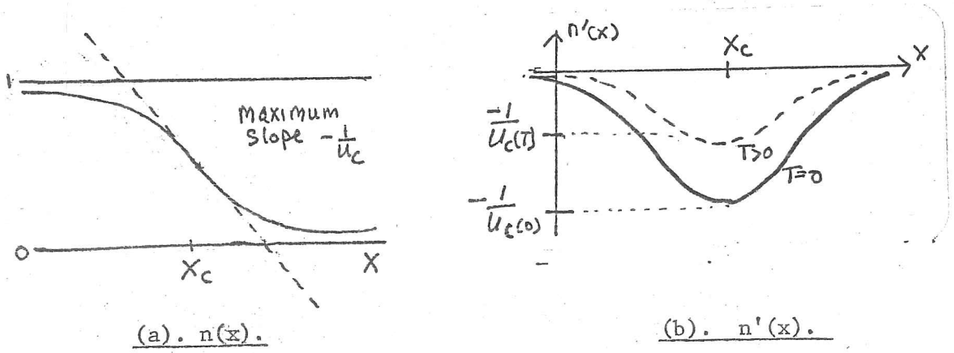
4.2 Character and Stability of Solutions of the Mean Field Equations

For the case $\Delta(\omega) = \Delta$, the function $n(x)$ (4.1.19) is given by

$$n(x) = \frac{1}{\pi}\int_{-\nu}^{\nu} d\omega \left(\frac{-1}{e^{\beta\omega}+1}\right)' \cot^{-1}(x/\Delta) \qquad (4.2.1)$$

$$= \pi^{-1}\cot^{-1}(x/\Delta) \quad (T=0) \qquad (4.2.2)$$

For large temperatures $T >> \Delta$, $n(x) \sim (1 + \exp(\beta x))$ for $|x| < T$, returning to (4.2.2) asymptotically. The cases considered here will be those where $\Delta(\omega)$ has little dependence on band structure effects, and, as for the case $\Delta(\omega) = \Delta$, $n'(x)$ is characterised by a unique minimum at $x = x_c$, where $n'(x_c) = -1/U_c$ (Fig. (4.1)):



(a). $n(x)$. (b). $n'(x)$.

Fig. (4.1) : Form of $n(x)$, $n'(x)$.

This form is found for most 'reasonable' band structures, though no doubt pathological forms of $\Delta(\omega)$ giving rise to more than one minimum of $n'(x)$ can be constructed. At T=0 $U_c \sim \pi\Delta(0)$; U_c increases with temperature: for $T >> \Delta(0)$, $U_c \simeq 4T$.

The HF equations, where $E_\uparrow^{eff} = x$, $E_\downarrow^{eff} = y$, are

$$x = E_d - C\,n(x) + (u-C)\,n(y)$$
$$y = E_d - C\,n(y) + (u-C)\,n(x) \qquad (4.2.3)$$

The solutions are best illustrated graphically (Fig. 4.2)

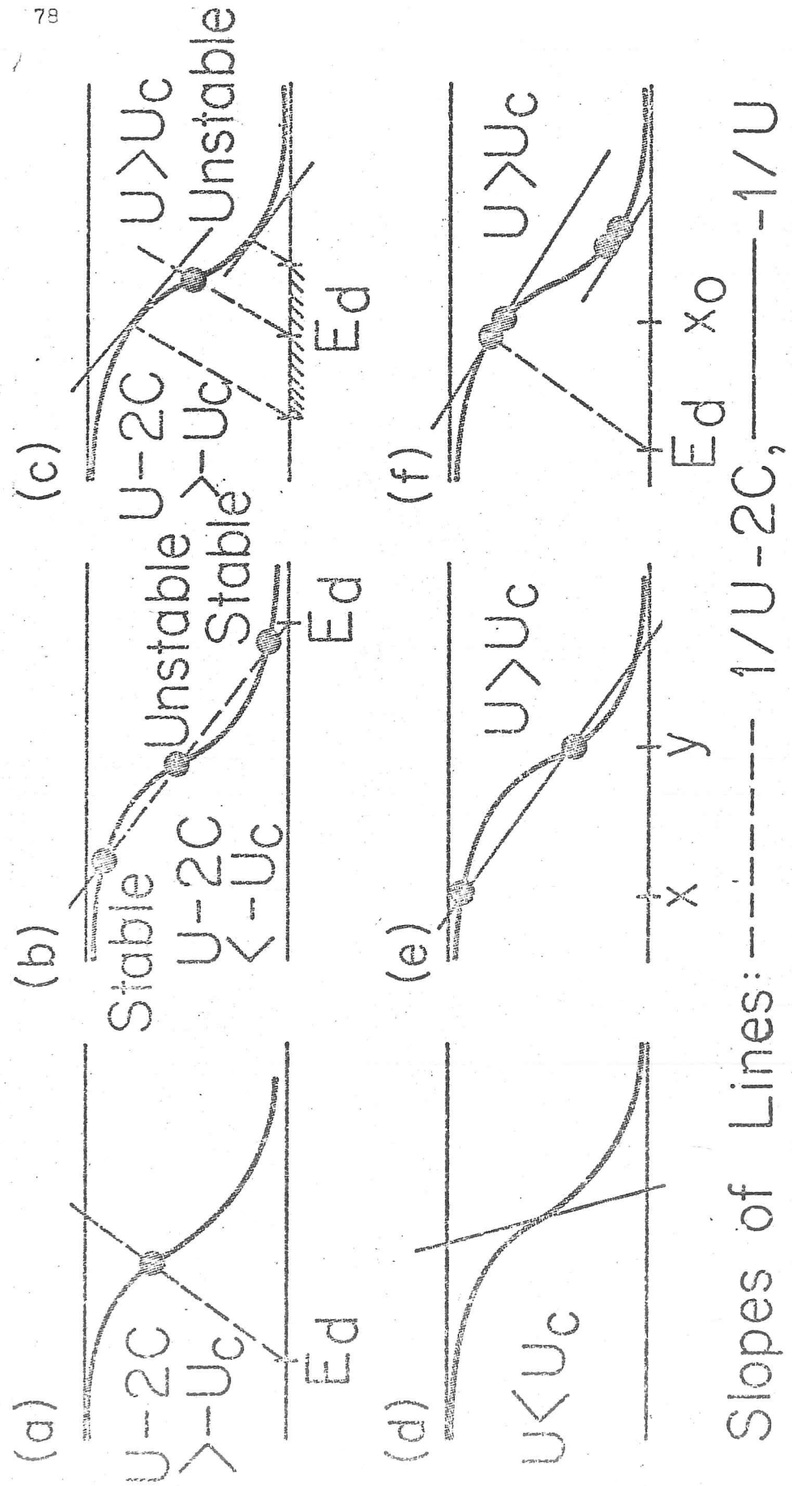


Fig. (4.2). Graphical solution of the HF equations (see text).

There is always a non-magnetic solution x=y:

$$X = E_d + (u-2c)\, n(x) \tag{4.2.4}$$

This is solved graphically in Fig. (4.2(a)). For $U-2C > -U_c$, this solution is unique; for $U-2C < -U_c$, there are multiple solutions in a certain range of E_d. In particular, if such solutions exist, $1 - (U-2C)n'(x) < 0$ when x is given by the intermediate solution (Fig. (4.2(b))). The condition for a solution to be <u>locally</u> stable is that it is a minimum of the free energy functional F(x,y) (4.1.25). To test whether this is so, the second derivatives of F at the solution must be examined. It is convenient to take derivatives in the directions $u = (x+y)/\sqrt{2}$, $v = (x-y)/\sqrt{2}$. At a stationary point of F(x,y), (x=y):

$$\begin{aligned} F_{uu} &= -n'(x)\,(1-(u-2c)n'(x)) \\ F_{uv} &= F_{vu} = 0 \\ F_{vv} &= -n'(x)\,(1+un'(x))\,. \end{aligned} \tag{4.2.5}$$

For stability, both F_{uu} and F_{vv} must be positive. U_c was defined so that $0 < -U_c n' \leq 1$; when $U-2C > -U_c$, the non-magnetic solution is unique, and stable in the x=y direction. If the condition $1 + Un'(x) > 0$ is also satisfied, the solution is locally stable. If $1 + Un'(x) < 0$, it is locally unstable against magnetism: this is only possible if $U > U_c$ (Fig, (4.2(c)); then it can be seen that there is a range of the parameter E_d where no locally stable non-magnetic solutions exist. If $U-2C < -U_c$, and $U < U_c$, solutions are stable against magnetism, but multiple non-magnetic solutions may exist; if they do, those with $1 - (U-2C)n'(x) < 0$ are not stable.

Such an unstable solution lies between two stable ones (Fig.(4. (b)); as E_d is moved through the range $(-\infty,\infty)$, a discontinuity will occur with a first order transition between two different locally stable non-magnetic solutions. In the remaining region of parameter space, $U-2C < -U_c$, $U > U_c$, non-magnetic solutions may be unstable in either or both directions.

Magnetic solutions, $x \neq y$, must now be examined. Taking the difference between the two HF equations (4.2.3):

$$x + Un(x) = y + Un(y) \quad . \tag{4.2.6}$$

Figures (4.2(d)), (4.2(e)) show that magnetic solutions only exist if $U > U_c$. For $U-2C > -U_c$, $U > U_c$, magnetism is stable at intermediate E_d. At the special value U=C, the HF equations for the two spin directions are decoupled, and the free energy functional can be written

$$F(x,y) = \tilde{F}(x) + \tilde{F}(y) \quad . \tag{4.2.7}$$

The conditions $U = C$, $U > U_c$, imply that $U-2C < -U_c$, so there is a region of the parameter E_d in which there are multiple non-magnetic solutions. Suppose $(x,y)=(a,a)$, $(x,y)=(b,b)$ are two different locally stable non-magnetic solutions, and E_d is precisely at that value where they are degenerate. Then $(x,y)=(a,b)$ is <u>also</u> a solution of the HF equation, and has the same free energy. Evidently, the line U=C is the dividing line where the behaviour as a function of E_d switches from a discontinuity between two non-magnetic solutions at some critical value, to the appearance of an intermediate magnetic solution. This can be seen in more detail by examination of the free energy surfaces for the solutions (a,a), (b,b), (a,b) in the neighbourhood of $U = C$ in the (E_d,U) plane, when $C > U_c$.

The solutions may be analytically continued to nearby values of E_d and U. Expanding the free energy of a solution $(x(E_d,U), y(E_d,U))$ about given values of E_d and U:

$$\left.\frac{\partial F}{\partial u}\right)_{E_d} = n(x)n(y) \quad ; \quad \left.\frac{\partial F}{\partial E_d}\right|_u = n(x) + n(y) \quad . \tag{4.2.8}$$

Hence

$$\frac{dF}{du} = n(x)n(y) + (n(x)+n(y))\frac{dE_d}{du} \quad . \tag{4.2.9}$$

Suppose $n(a) > n(b)$;

$$\frac{dF(a,a)}{du} = \left(n(a)^2 + 2n(a)\frac{dE_d}{du}\right); \quad \frac{dF(a,b)}{du} = \left(n(a)n(b) + (n(a)+n(b))\frac{dE_d}{du}\right) \text{ etc.} \tag{4.2.10}$$

At $U = C$, $E_d = E_d^*$ (where $a + Cn(a) = b + Cn(b) = E_d^*$), $F(a,a) = F(b,b) = F(a,b)$, that is, all <u>three</u> solutions are degenerate. The lines $E_d(U)$ along which <u>two</u> of these remain degenerate (i.e., $F(a,a) = F(b,b)$, $F(a,a) = F(a,b)$ and $F(b,b) = F(a,b)$) must be examined:

$$\begin{aligned} F(a,a) = F(b,b) &\rightarrow \frac{dE_d}{du} = -\tfrac{1}{2}(n(a)+n(b)) \\ F(a,a) = F(a,b) &\rightarrow \quad " \quad = -n(a) \\ F(b,b) = F(a,b) &\rightarrow \quad " \quad = -n(b). \end{aligned} \tag{4.2.11}$$

The sectors of the plane around $E_d = E_d^*$, $U = C$, where each of the solutions remain <u>globally</u> stable, are shown in Fig (4.3)

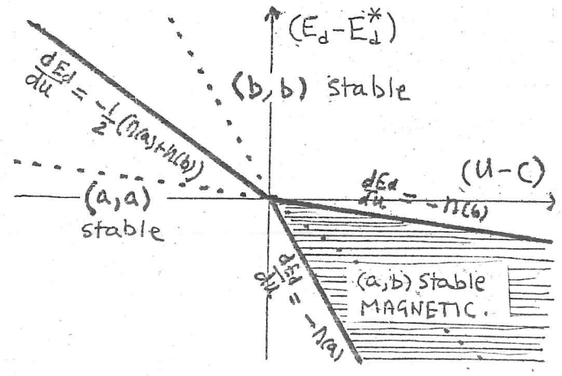


Fig. (4.3)
Global stability of HF solutions (x,y) in the (E_d,U) plane.
(for $C > U_c$).

As the three solutions are distinct, the stability boundaries dividing the (E_d,U) plane in the neighborhood of (E_d^*,C) into three sectors are lines of first order discontinuities of the globally stable solution. The magnetic solution is globally stable in the sector $-n(b)\delta U > \delta E_d > -n(a)\delta U$, $\delta U > 0$; as $U = C \rightarrow U_c$, the two non-magnetic solutions (a,a), (b,b) merge, and the angle between the upper and lower boundaries

of the magnetic section shrinks to zero. At $U = C = U_c$, the first order boundaries of the magnetic sector come together into a cusp at (E_d^*, U_c).

The condition $U > C$ for the existence of a globally stable magnetic solution is easy to understand. It is the condition for the effective coupling, U-C, between opposite spin electrons to be repulsive, a prerequisite for magnetism.

The behaviour of the globally stable solution as E_d is varied from $-\infty$ to $+\infty$ is shown as a function of U and C in the (U,C) half-plane (Fig.(4.4)).

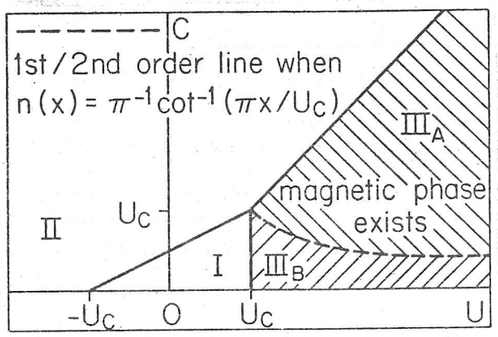


Fig.(4.4)
Behaviour of the stable HF solution as E_d is raised.
I. non-magnetic, continuous.
II. non-magnetic, discontinuous.
III. magnetic solution intervenes; A- first order transition; B- second order.

In region I, the solution is non-magnetic, and varies continuously with E_d. In region II, there is a discontinuity between two non-magnetic solutions at some intermediate E_d. In region III, a magnetic region intervenes between regions of non-magnetic solutions. The remaining question to settle is the nature of the magnetic/non-magnetic 'phase' boundaries. As this is a change-involving a 'broken symmetry,' it can be either continuous or discontinuous. Along the line $U = C$, $U > U_c$, the change is seen to be first order; the line $U = U_c$, $C < U_c$, is a line along which the non-magnetic solution is a solution with $x-\dot{y} = 0$ of the magnetic equation (4.2.5), and hence the change is second order on this line. The first/second order dividing line obviously terminates at $U = C = U_c$. (In principle, there will be two

boundaries in the (U,C) plane, one marking the criterion for the upper magnetic boundary to be first or second order, and the other representing the lower boundary. If the band structure has particle-hole symmetry, ($\Delta(\omega) = \Delta(-\omega)$), these two boundaries are identical.)

A critical solution, where the magnetisation goes continuously to zero, always exists, and satisfies $1+Un'(x)=0$ (Fig.(4.2(f))). A necessary condition for the transition to be second order is that this solution is locally stable. It is a sufficient condition if at most one distinct locally stable magnetic solution exists for any E_d. (Solutions (b,a) are not distinct from (a,b), neither are those others rotationally degenerate with (a,b).) Along the lines $U = C$, ($U > U_c$), where the transition is first order, and $U = U_c$, ($C > U$), where it is second order, the condition that only one locally stable magnetic solution exists is satisfied (due to the simplifying assumption that $n'(x)$ has a unique minimum). By continuity, this is true in the neighbourhood $U = U_c + \delta U$, $C = U_c + \delta C$. The criterion for stability of the critical solution is found by examining higher derivatives of F, as the determinant of second derivatives vanishes at that point. The condition for the critical solution to be stable turns out to be:

$$-\frac{n'''(x_0)}{(n''(x_0))^2} < \frac{3}{2}U \cdot \frac{U-2C}{U-C} \qquad (4.2.12)$$

where $(1 + Un'(x_0))=0$. As n'' vanishes at x_c, the stability condition around $U \simeq C \simeq U_c$ is found by expanding around x_c, and is universally (i.e, independent of the detailed form of $n(x)$):

$$C < U_c - 2\delta U \quad . \qquad (4.2.13)$$

Away from this region, the criterion depends on the particular form of $n(x)$. For the case $\Delta(\omega)$ = const, T = 0, the condition is

$$C < UU_c/(3U-2U_c) \qquad (4.2.14)$$

(see Fig. (4.4)). For large U, this asymptotically becomes $C < U_c/3$.

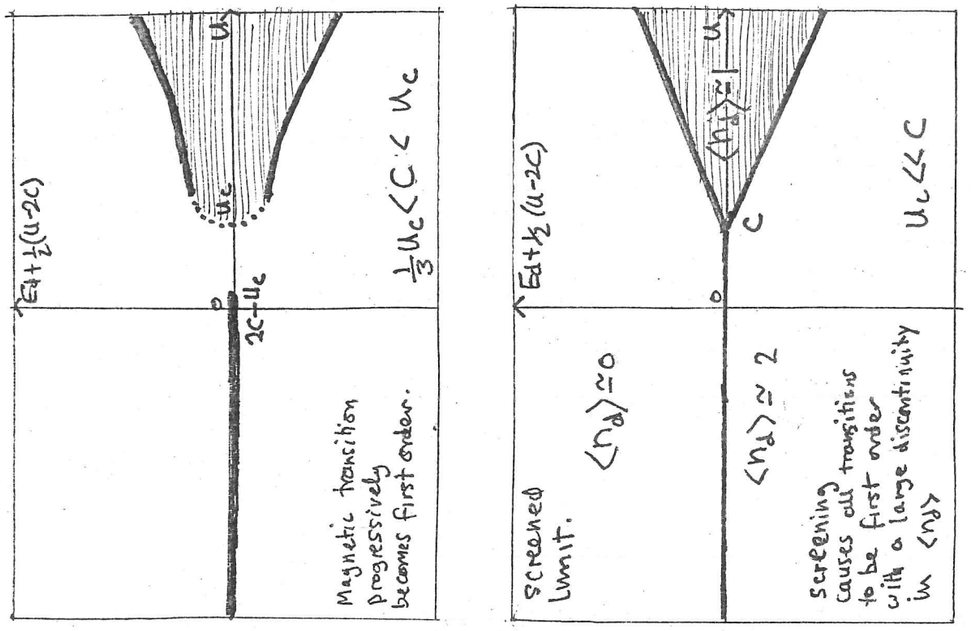


Fig. (4.5). Mean-field phase diagrams in the presence of screening. (see text.)

For large T, the condition (4.2.12) becomes less stringent, but approaches (4.2.14) for large U, as n(x) is essentially unaffected by finite temperature for $|x| > T$.

If the effect of finite bandwidth is examined, it is found that n(x) must eventually behave as (constant)/x^2 for x >> bandwidth. In that case, the stability condition for large U becomes $C < U/10$, even less stringent than (4.2.14).

Detailed examination of the canonical case Δ constant, T = 0 to test whether the necessary condition of a stable critical solution was sufficient to guarantee a second order transition, showed it was in that case, as there were no secondary stable magnetic solutions. It is plausible that this will be true for all cases where $n'(x)$ has a unique minimum, as this simple form would seem to preclude the existence of many magnetic roots of the HF equations (at least three distinct magnetic solutions are necessary for two to be stable). It is thus concluded that $C = U_c/3$ is indeed a lower bound for first order magnetic 'phase boundaries.'

The 'phase diagrams' for the globally stable mean field solutions are shown in Fig. (4.5) . . They are plotted in the (E_d,U) plane for a series of values of the boson coupling constant C. The vertical coordinate is chosen as $(E_d+\frac{1}{2}(U-2C))$ so the horizontal axis is a line of particle/hole symmetry (that is, if $\Delta(\omega) = \Delta(-\omega)$). Of main interest are the limiting cases $U_c >> C$ (standard Anderson model), and $C >> U_c$. The amusing (but largely irrelevant) 'crossover' behaviour is also shown. The important new feature is the existence of first order discontinuities in the physical positive U region, at which two different stable HF configurations are degenerate.

4.3 Collective Excitation Modes in the Random Phase Approximation (RPA)

It is instructive to use the RPA to examine the spectrum of collective excitations about HF solutions, and in particular to find the stability conditions which ensure that unstable modes with imaginary frequency do not exist.

The effective Hamiltonian may be diagonalised around a general HF solution, and written as

$$H^{eff} = \text{const.} + \sum_{i\sigma} \varepsilon_{i\sigma} c^{\dagger}_{i\sigma} c_{i\sigma} + \sum_{q} \omega_q b^{\dagger}_q b_q \qquad (4.3.1)$$

where

$$c_{\delta\sigma} = \sum_{i\sigma} u_{i\sigma}\, c_{i\sigma} \qquad (4.3.2)$$

The RPA equations are obtained by linearising the equations of motion of a particle-hole pair:

$$[H, c^{\dagger}_i c_j]^{RPA} = H^{RPA}_{pq,ij}\, c^{\dagger}_p c_q \qquad (4.3.3)$$

where the approximation is the replacement:

$$c^{\dagger}_i c^{\dagger}_q c_q c_j \simeq \langle c^{\dagger}_i c_j\rangle c^{\dagger}_p c_q + \langle c^{\dagger}_p c_q\rangle c^{\dagger}_i c_j - \langle c^{\dagger}_p c_j\rangle c^{\dagger}_i c_q - \langle c^{\dagger}_i c_q\rangle c^{\dagger}_p c_j \qquad (4.3.4)$$

The RPA eigenvalue equations for the collective modes are easily solved, and the results are stated here. First a 'generalised susceptibility' will be defined for the impurity orbital:

$$\chi_{\sigma\sigma'}(\omega) = \sum_{ij} \frac{|u_{i\sigma}|^2 |u_{j\sigma'}|^2}{\omega - (\varepsilon_{i\sigma} - \varepsilon_{j\sigma'})} \left(\langle n_{i\sigma}\rangle - \langle n_{j\sigma'}\rangle\right) \qquad (4.3.5)$$

$\chi_{\sigma\sigma'}(\omega) = \chi_{\sigma'\sigma}(-\omega)$, and with some manipulation using the definition of $n(x)$ (4.1.19), it can be shown that

$$\chi_{\sigma\sigma'}(0) = -\left[n(E^{eff}_{\sigma}) - n(E^{eff}_{\sigma'})\right] \Big/ \left(E^{eff}_{\sigma} - E^{eff}_{\sigma'}\right). \qquad (4.3.6)$$

If $E^{eff}_{\sigma} = E^{eff}_{\sigma'}$, this reduces to $-n'(E^{eff}_{\sigma})$.

On solving the RPA eigenvalue equations, four sets of collective modes are found. There is a conjugate doublet of modes, related by time reversal, involving pairs $c^{\dagger}_{i\sigma} c_{j-\sigma}$, with eigenvalue equation

$$1 - U\chi_{\sigma-\sigma}(\omega) = 0 \qquad (4.3.7)$$

The other two modes mix $c^{\dagger}_{i\sigma} c_{j\sigma}$ and $b^{\dagger}_q$ with eigenvalues given by

$$1 \pm [U - C(\omega)] \left[\frac{\chi_{\uparrow\uparrow}\chi_{\downarrow\downarrow}}{(1 - C(\omega)\chi_{\uparrow\uparrow})(1 - C(\omega)\chi_{\downarrow\downarrow})} \right]^{1/2} \qquad (4.3.8)$$

where

$$C(\omega) = 2g^2 \sum_q |d_q|^2 \omega_q / (\omega_q^2 - \omega^2) \; . \qquad (4.3.9)$$

$C(\omega)$ is the ω-dependent electron-electron attraction mediated by the bosons. The effective coupling constant C entering in the HF equations is the static value $C(0)$.

In the non-magnetic case, $\chi_{\sigma\sigma'} \equiv \chi$, (4.3.6) and (4.3.7) reduce to a triplet of spin fluctuation modes with eigenvalue equation $1-U\chi(\omega)=0$, and (unnormalised) eigenstates $\sum_{\sigma\sigma'} U \vec{\sigma}_{\sigma\sigma'} \Phi_{\sigma\sigma'}(\omega)$, where

$$\Phi_{\sigma\sigma'}(\omega) = \sum_{ij} \frac{u^*_{i\sigma} u_{j\sigma'}}{\omega - (\varepsilon_i - \varepsilon_j)} \left(c^{\dagger}_{i\sigma} c_{j\sigma'} - \langle c^{\dagger}_{i\sigma} c_{j\sigma'}\rangle \right) . \qquad (4.3.10)$$

There is also a set of singlet charge fluctuation modes with eigenvalue equation $1 - (2C(\omega)-U)\chi(\omega) = 0$, and eigenstates

$$(2C(\omega) - U) \sum_{\sigma} \Phi_{\sigma\sigma} \cdot - 2g \sum_q \left(\frac{\alpha_q}{\omega - \omega_q} b_q + \frac{\alpha^*_q}{\omega + \omega_q} b^{\dagger}_q \right) \qquad (4.3.11)$$

Since $\chi(\omega) = \chi(-\omega)$, (from (4.3.5)) $\chi(i\alpha) > \chi(0) > 0$; also $0 < C(i\alpha) < C$, hence the stability conditions (i.e., no imaginary eigenvalues) are $1 + Un'(E^{eff}) > 0$ for spin fluctuation modes, and $1-(U-2C)n'(E^{eff}) > 0$ for charge fluctuation modes. These are just the criteria derived from the previous variational treatment of the free energy (4.2.5).

In the magnetic case, the spin modes split into a singlet parallel to $\langle \vec{s}_d \rangle$ and a perpendicular doublet. Owing to the rotational degeneracy of the broken-symmetry magnetic solutions, there must be a set of zero energy 'Goldstone boson' modes corresponding to infinitesimal rotations of $\langle \vec{s}_d \rangle$; these arise from the perpendicular $\omega = 0$ doublet; the condition for zero energy modes is $1-U\chi_{\sigma-\sigma}(\omega) = 0$; (4.3.6) then implies that

$$E_{\sigma}^{eff} + U n(E_{\sigma}^{eff}) = E_{-\sigma}^{eff} + U n(E_{-\sigma}^{eff}) \qquad (4.3.12)$$

This is just the condition (4.2.6) that magnetic solutions must satisfy. The other two modes mix charge and spin modulus excitations. Equation (4.3.7) implies that when $U > C$, at least one of these two sets of modes is stable, and magnetic solutions in this region are either minima or saddle-points.

To summarise: the RPA stability criteria reproduce those derived earlier from the variational procedure: non-magnetic minima correspond to HF solutions that are stable in RPA. Magnetic 'minima' are not truly stable, as a zero energy Goldstone mode exists.

4.4 Discussion of the Mean Field Theory Results; Corrections to Mean Field Theory.

On examining the physical positive U half-plane of the mean field phase diagrams (Fig. (4.5)), one sees that the important new features due to the bosons are the discontinuities in the mean displacement of the boson field, and hence $\langle n_d \rangle$, as the bare level E_d is raised. Such discontinuities are of course artifacts of the mean field approximation; the problem they raise may be resolved by going to the next level of approximation, the Born-Oppenheimer approximation. In this approximation, the dynamics of the bosons are reincluded in the theory, and the boson field is treated as moving in an effective potential derived from the adiabatic response of the electrons, so they are always in equilibrium with the instantaneous displacement of the boson field.

If there is a single minimum of the effective potential, the only modification of the mean field results is the inclusion of the boson field motion around the potential minimum corresponding to the mean field solution; since the electron-boson coupling is linear, there is no modification of the boson frequencies, and in the case of phonons at temperatures below the Debye temperature ω_D, this motion is just the zero-point motion.

If there is a second minimum of the effective potential, but with a much higher energy than the first, this picture will not be affected. However, as this second minimum is lowered with respect to the first and eventually becomes the true minimum, mean field theory spuriously predicts a discontinuity as the mean boson amplitude jumps from one minimum of the potential to the other. In reality, when the two minima are close in energy, the boson field will tunnel between them

and the discontinuous crossover of mean field theory will be smoothed out over a range of energy given by the characteristic tunnelling frequency.

In the Born-Oppenheimer approximation, the boson Hamiltonian becomes

$$H = \sum_q \omega_q b_q^\dagger b_q + V\left(g \sum_q \alpha_q (b_q + b_q^\dagger)\right) \qquad (4.4.1)$$

where $V(x)$ is given by

$$V(x) = \langle \bar{H}(x) \rangle_{\bar{H}(x)} , \qquad (4.4.2)$$

$$\bar{H}(x) = (E_d + x) \sum_\sigma n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{k\sigma} V_{kd} c_{k\sigma}^\dagger c_{d\sigma} + h.c. \qquad (4.4.3)$$

As x is raised $\langle n_d \rangle$ will change from (say) $\langle n_d \rangle \simeq 1$ to $\langle n_d \rangle \simeq 0$ over a range Δ around $x = x_0 \simeq -E_d$; outside this narrow crossover range $V(x) \simeq (x - x_0)$ for $x \ll x_0$ and 0 for $x \gg x_0$.

The general boson problem (4.4.1) is rather intractable as it stands, being a complicated many-body problem involving strongly non-linear couplings between all the boson modes. Its physics might be described by treating low frequency modes as experiencing a fluctuating time dependent potetial due to the motion of the higher frequency modes. However, in the case that the bosons are phonons, specialising to the case of Einstein phonons without dispersion reduces the problem to a manageable simple quantum mechanical problem of motion of a single particle in a double well.

The Hamiltonian (4.4.1) becomes

$$H = \omega_D b^\dagger b + V(g(b + b^\dagger)) \quad ; \qquad (4.4.4)$$

or, using first-quantised operators:

$$\phi = \frac{b^\dagger + b}{\sqrt{2}} \quad ; \quad \Pi = \frac{b - b^\dagger}{\sqrt{2}\, i} \quad ; \quad [\Pi, \phi] = -i \qquad (4.4.5)$$

$$H = \omega_D (\Pi^2 + \phi^2) + V(\sqrt{2} g \phi)$$
$$= \omega_D (\Pi^2 + U(\phi)) \qquad (4.4.6)$$

where the potential $U(\phi)$ is approximately

$$U(\phi) \simeq \phi^2 + \frac{\sqrt{2}\,|g|}{\omega_D} (\phi - \phi_0)\, \theta(\phi_0 - \phi) \qquad (4.4.7)$$

As E_d (and hence ϕ_0) varies , the potential takes the forms shown in Fig. 4.6. Also shown is the ground state wavefunction. The cusp of the

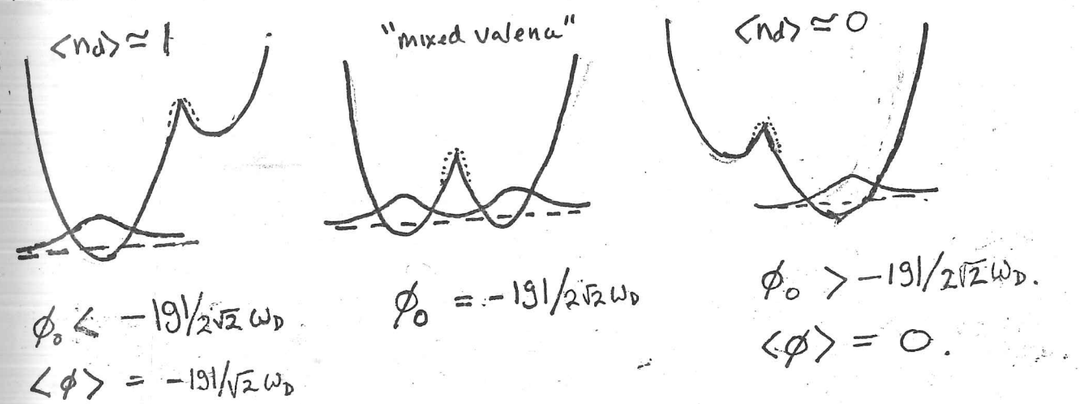


Fig.(4.6) The approximation (4.4.7) to $U(\phi)$ for increasing ϕ_0, showing the ground state wavefunction changing valence. (..... = true $U(\phi)$).

potential at ϕ_0 is of course an artifact of the limiting form (4.4.7), and is in fact smoothed out over a range $\delta\phi \simeq \Delta/g$ around ϕ_0. This smoothing can be neglected when $C = 2g^2/\omega_D$ is much greater than Δ. In the other extreme $C \ll \Delta$ the smoothing correction dominates, and the potential $U(\phi)$ now only has a single minimum.

In the tunnelling limit $C \gg \Delta \gg \omega_D$, the tunnelling frequency may be estimated variationally using a trial wavefunction that is a superposition of the ground state wavefunctions appropriate to each minima. This is done in Appendix 4B; this procedure is likely to be ; asymptotically exact as $\omega_D \to 0$. This tunnelling frequency can be expressed as a "valence fluctuation temperature" T_{vf} of order

$$T_{vf} \simeq (\omega_D C)^{1/2} \langle 0 | 1 \rangle \qquad (4.4.8)$$

where $\langle 0 | 1 \rangle$ (=exp- C/ω_D) is the overlap of the boson ground states

corresponding to the two valences. The form (4.4.8) may also be expected to hold when there is slight dispersion of the boson frequencies around ω_D.

Estimation of the tunnelling frequency T_{vf} in the case of the Tomonaga boson field would be much more difficult, but, as discussed later, it turns out that the phenomenon of tunnelling is not relevant to these screening modes, since after the renormalising effects of the high frequency part of the Tomonaga spectrum have been taken into account, $C^{eff} \lesssim \Delta^{eff}$, and the effective Born-Oppenheimer potential has only a single minimum.

It is instructive to examine the spectrum of $G_d(\omega)$ in Hartree-Fock approximation in the $C \gg \Delta$ (tunnelling) limit . As discussed earlier (section 2.6) the true spectrum will resemble the Hartree-Fock result averaged over spin. Here, when the additional degeneracy between stable solutions of different valence is encountered, the correponding prescription is to take a combination of the two solutions, in proportions that determine the actual non-integral valence. At T=0, these solutions must be modified at the Fermi-level in accordance with the sum rule (2.5.35), (2.6.11) which is still valid.

A sequence of such spectra as E_d is raised is shown in Fig. (4.7). At the valence crossover, one finds two Hartree-Fock resonances at $\pm\frac{1}{2}C$ with widths Δ, equally spaced above and below the Fermi level, with approximate weights $(1 - \langle n_d \rangle)$ and $\frac{1}{2}\langle n_d \rangle$ respectively. (There is a second resonance at a large energy of order U that contains the remaining weight of $\frac{1}{2}\langle n_d \rangle$). Because of the T=0 sum rule (2.6.11), i.e.:

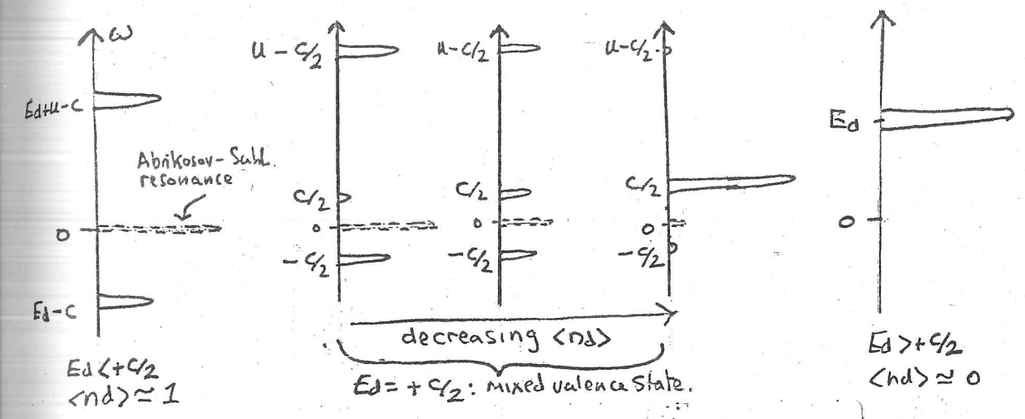


Fig. (4.7) HF spectrum of $G_d(\omega)$ as E_d rises. Behaviour of the Abrikosov-Suhl resonance is also depicted. (T=0).

$$\mathrm{Im}\, G_d(0) = \Delta^{-1} \sin^2(\pi\langle n_d \rangle/2), \qquad (4.4.9)$$

the height of the Fermi surface resonance at T=0 is fixed in accordance with the mean valence. There are two fluctuation processes that may determine the width of the Fermi surface resonance: one is the the valence fluctuation process, controlled by the characteristic tunnelling frequency T_{vf}; the other is the Kondo spin-flip process while the system is in the magnetic valence state $n_d \simeq 1$. This latter effect will dominate provided $T_K \gg T_{vf}$, i.e., as long as the lifetime of the $n_d \simeq 1$ valence state is long enough for the Kondo processes to occur; the width of the resonance will then be the T_K appropriate to the magnetic HF solution. If on the other hand, $T_{vf} \gg T_K$, the width will be T_{vf}, and in fact the spin fluctuation time should also be T_{vf}^{-1}, since a valence fluctuation will wipe out any memory of the previous spin orientation.

Reference.

Anderson P. W. (1961); Phys. Rev. 124, 41.

Appendix 4A Free Energy of the Spinless Anderson Model.

The spinless fermion Anderson model is

$$H = \sum_k \varepsilon_k c_k^\dagger c_k + E_d c_d^\dagger c_d + \sum_k V_{kd} c_k^\dagger c_d + h.c. \tag{4.A.1}$$

the Green's function equations of motion are easily solved (Anderson (1961)):

$$G_{dd}(\omega) = \left(\omega - E_d - \sum_k \frac{|V_{kd}|^2}{\omega - \varepsilon_k}\right)^{-1} \tag{4.A.2}$$

$$G_{kd}(\omega) = \frac{V_{kd}}{\omega - \varepsilon_k} G_{dd}(\omega) \tag{4.A.3}$$

$$G_{kk'}(\omega) = \frac{\delta_{kk'}}{\omega - \varepsilon_k} + \frac{V_{kd}}{\omega - \varepsilon_k} G_{dd}(\omega) \frac{V_{dk'}}{\omega - \varepsilon_{k'}} \tag{4.A.4}$$

The free energy may be constructed using the Hellmann-Feynman theorem (coupling constant integration):

$$\begin{aligned} F &= F\left(\sum_k \epsilon_k n_k + E_d n_d\right) + \int_0^1 d\lambda\, V_{kd} \langle c_d^\dagger c_k \rangle_{H_0 + \lambda H'} + h.c \\ &= F_0(E_d) + \frac{1}{2\pi i} \oint \frac{d\omega}{e^{\beta\omega}+1} \int_0^1 d\lambda \cdot 2\lambda \sum_k \frac{|V_{kd}|^2}{(\omega - \varepsilon_k)} \cdot \left(\omega - E_d - \lambda^2 \sum_k \frac{|V_{kd}|^2}{(\omega - \varepsilon_k)}\right)^{-1} \end{aligned} \tag{4.A.5}$$

Since E_d may likewise be treated as a coupling constant

$$F = F_0(E') + \frac{1}{2\pi i} \oint_\Gamma \frac{d\omega}{e^{\beta\omega}+1} \ln\left(\frac{\omega - E_d - \sum_k \frac{|V_{kd}|^2}{\omega - \varepsilon_k}}{\omega - E'}\right) \tag{4.A.6}$$

The contour Γ encloses the real axis. This contour may always be closed 'at infinity', even though the integrand has a cut along the real axis, if the integral without closure exists. (Fig. (4.8)).

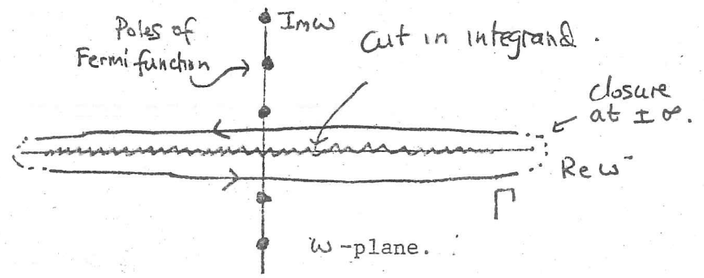


Fig. (4.8) The contour Γ in the ω-plane.

Appendix 4B: Asymptotic Evaluation of the Tunnelling Frequency of a Particle in the Double Harmonic Well of Section 4.4 .

The harmonic oscillator Hamiltonians $H_{\pm}(x)$ are defined by:

$$H_{\pm}(x) = -\frac{d^2}{dx^2} + (x \mp a)^2 - 1 \qquad (4.B.1)$$

The ground states are given by

$$\psi_{\pm}(x) = N \exp -\tfrac{1}{2}(x \mp a)^2 \qquad (4.B.2)$$

where N is a normalisation constant. The full energy level spectrum is given by $E_n = 2n$, the parity of the wavefunctions is $(-1)^n$.

The full Hamiltonian H will be defined by

$$H(x) = \theta(x) H_+(x) + \theta(-x) H_-(x) \; . \qquad (4.B.3)$$

The potential is shown in Fig. 4.7

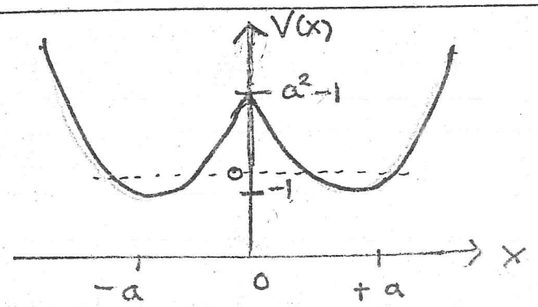


Fig. (4.7) Potential of the Hamiltonian (4.B.3).

In the limit a=0, the spectrum of H is that of $H_{\pm}$; in the limit $a \to \infty$ the spectrum is the product of that of H_+ and H_- - every level is now a doublet with one state of each parity on reflection $x \to -x$. The spectrum of H as a function of a is shown schematically in Fig 4.8 :

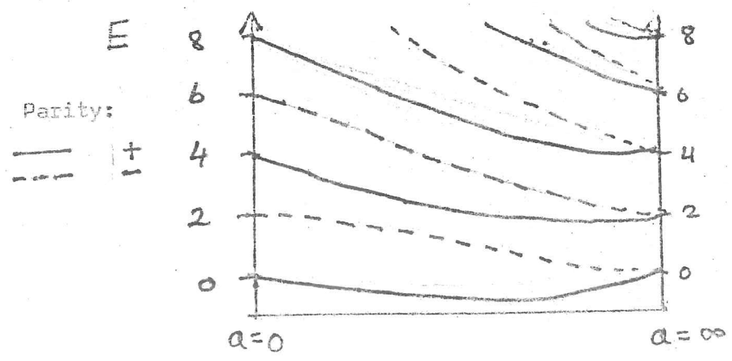


Fig. (4.8) Spectrum of H as a function of a.

In the limit $a \to \infty$ the ground state, with E_0 giving the tunnelling energy, is well separated from the first excited state of even parity at E = 2.

A variational estimate of E_0 may be obtained using a superpostion $|0\rangle$ $\psi_+ + \psi_-$ as an approximation to the ground state. Knowledge of the lowest excited level of even parity will allow a lower as well as an upper bound to E_0 to be obtained for large a. The following integrals are evaluated asymptotically as $a \to \infty$:

$$\langle 0|0\rangle = \int_{-\infty}^{\infty} dx \; \psi_+^2(x) + \psi_-^2(x) + 2\psi_+(x)\psi_-(x)$$
$$= 2(1+\exp -a^2) \int_{-\infty}^{\infty} \exp -x^2 \, dx$$
$$= 4\sqrt{\pi}\,(1+\exp -a^2) . \qquad (4.B.4)$$

To evaluate $\langle 0|H|0\rangle$, $\langle 0|H^2|0\rangle$ it is useful to note

$$\langle 0|H^n|0\rangle = 2\int_0^{\infty} dx \, (\psi_+ + \psi_-) H_+^n (\psi_+ + \psi_-) \qquad \text{(by symmetry)} \qquad (4.B.5)$$

$$H_+\psi_+ = 0 \; ; \; H_+\psi_- = -4ax\psi_- \; . \qquad (4.B.6)$$

Then:

$$\langle 0|H|0\rangle = -8a \exp -a^2 \int_0^{\infty} dx \; x \exp -x^2 (1+\exp -2ax)$$
$$= -8a \exp -a^2 \left(\tfrac{1}{2} + \tfrac{1}{4a^2} + O\left(\tfrac{1}{a^4}\right)\cdots\right) \qquad (4.B.7)$$

$$\langle 0|H^2|0\rangle = 32a^2 \int_0^{\infty} dx \; x^2 \exp -x^2 \, (1+\exp -2ax) \; .$$
$$= 32\,a^2 \exp -a^2 \left(\tfrac{1}{2}\sqrt{\pi} + \frac{1}{4a^3} + O\left(\tfrac{1}{a^5}\right)\cdots\right) \qquad (4.B.8)$$

Thus:

$$J_1 \equiv \frac{\langle 0|H|0\rangle}{\langle 0|0\rangle} = -\frac{a}{\sqrt{\pi}} \exp -a^2 \left(1 + \frac{1}{8a^2} + O\left(\frac{1}{a^4}\right)\cdots\right) \qquad (4.B.9)$$

$$J_2 \equiv \frac{\langle 0|H^2|0\rangle}{\langle 0|0\rangle} = \frac{a}{\sqrt{\pi}} \exp -a^2 \left(4\sqrt{\pi}\,a + \frac{2}{a^2} + O\left(\frac{1}{a^4}\right)\cdots\right) . \qquad (4.B.10)$$

J_1 immediately gives an upper bound to E_0. A lower bound is given by considering

$$\langle 0|(H-E_0)(H_1-E_1)|0\rangle = \sum_n |a_n|^2 (E_n-E_0)(E_n-E_1) \geq 0 \qquad (4.B.11)$$

where E_0 is the ground state energy (exact) of H, and E_1 is the lowest (exact) excited level of the same symmetry. Writing in terms of J_1, J_2 :

$$J_2 - E_0(J_1-E_1) - E_1 J_1 \geq 0 \qquad (4.B.12)$$

$$E_0(E_1-J_1) \geq J_1(E_1-J_1) - (J_2-J_1^2) \qquad (4.B.13)$$

Now, <u>provided</u> $E_1 > J_1$:

$$E_0 \geq J_1 - \frac{J_2-J_1^2}{E_1-J_1} \qquad (4.B.14)$$

giving a lower bound to E_0.

Evaluating the bounds asymptotically as $a \to \infty$:

$$-\frac{a}{\sqrt{\pi}} \exp -a^2 \left(1+O\left(\frac{1}{a^2}\right)\right) \leq E_0 \leq -\frac{a}{\sqrt{\pi}} \exp -a^2 \left(2\sqrt{\pi}a+1+O\left(\frac{1}{a^2}\right)\right) \qquad (4.B.15)$$

This attempt to get a rigorous bound has not been entirely successful, as the upper bound is infinitely larger than the lower bound, reflecting the fact that the trial wavefunction has produced a J_2 exponentially larger than J_1^2. However, it is at least confirmed that the tunnelling is controlled by the exponentially small overlap factor. The estimate J_1 is indeed generally considered to be asymptotically correct in this type of problem (e.g., see Landau and Lifschitz, "Quantum Mechanics", Pergamon Press, Oxford (1965), p. 175).

Thus

$$E_0 \sim -a \langle \Psi_+ | \Psi \rangle . \qquad (4.B.16)$$

In dimensional quantities, $a = (\omega_0 h)^{\frac{1}{2}}$, where h is the barrier height, and ω_0 is the zero point energy of motion in the two disconnected wells.

CHAPTER FIVE

PERTURBATION EXPANSION OF THE SCREENED ANDERSON MODEL ABOUT THE ZERO HYBRIDISATION LIMIT

5.1 Role of the Bandwidth in the Anderson Model

When U = 0, the Anderson model may be exactly diagonalised:

$$\sum_{k\sigma} \varepsilon_k c^\dagger_{k\sigma} c_{k\sigma} + E_d \sum_\sigma c^\dagger_{d\sigma} c_{d\sigma} + \sum_{k\sigma} V_{kd} c^\dagger_{k\sigma} c_{d\sigma} + \text{h.c.} = \sum_{i\sigma} \varepsilon_i c^\dagger_{i\sigma} c_{i\sigma} \qquad (5.1.1)$$

The ground state energy shift due to hybridisation is

$$\Delta E_{gs} = 2 \cdot \lim_{\beta\to\infty} \frac{1}{2\pi i} \oint_\Gamma \frac{d\omega}{e^{\beta\omega}+1} \ln\left(\frac{\omega - E_d - \Sigma(\omega)}{\omega - E_d}\right) \qquad (5.1.2)$$

$$\Sigma(\omega) = \sum_k \frac{|V_{kd}|^2}{\omega - \varepsilon_k} = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega' \frac{\Delta(\omega')}{\omega - \omega'} . \qquad (5.1.3)$$

If $\Delta(\omega)$ is given by

$$\Delta(\omega) = \Delta \quad (-W < \omega < W)$$
$$= 0 \quad \text{otherwise} \qquad (5.1.4)$$

where W is the Anderson model bandwidth; the ground state energy shift ΔE_{gs} is logarithmically divergent in the $W \to \infty$ limit:

$$\Delta E_{gs} \sim \frac{2\Delta}{\pi} \ln W + f(E_d, \Delta) \qquad (5.1.5)$$

The divergent ground state energy may be subtracted and the $W \to \infty$ limit taken ; subsequent perturbation theory in U is perfectly well behaved as seen in the series of calculations by Yosida and Yamada (1970,1975), Yamada (1975a,b,1976). The $W\to\infty$ limit is the most convenient, as in that case the d-electron propagators have the particularly simple Lorentzian spectral density $\nu(\omega) = \Delta/((\omega-E_d)^2+\Delta^2)$.

Because of this, the only dependence on W in the $W\to\infty$ limit of the partition function of the full (finite U) Anderson model must be of the form

$$Z(E_d, U, \Delta, W) \simeq e^{-2\beta\frac{\Delta}{\pi}\ln W}\, \tilde{Z}(E_d, U, \Delta) \quad . \qquad (5.1.6)$$

From this form, it can be seen that expansion of Z in powers of Δ will lead to term by term logarithmic divergence in the $W\to\infty$ limit, both in the partition function expansion, and the free energy expansion that can be derived from it. However, these divergences are harmless, as they must cancel in any expansion of derivatives of the free energy, which are the physically relevant quantities. As the $W\to\infty$

($\Delta(\omega) = \Delta$) limit of the models is probably the simplest, or 'canonical' case, it will be treated by expansion in powers of Δ in the knowledge that the apparently disastrous term by term divergences in the partition function expansion are in fact of no consequence.

5.2 Perturbative Expansion of the Anderson Model Partition Function

Perturbative expansions may be based on the identity

$$Z(H^0+H'+H^2\cdots) \equiv Tr\left[e^{-\beta H^0} T_x \exp\left(-\int_0^1 H'(x)dx\right)\exp\left(-\int_0^1 H^2(x)dx\right)\cdots\right]$$
$$H'(x) = e^{\beta x H^0} H' e^{-\beta x H^0}. \qquad (5.2.1)$$

For the Anderson model, $H = H^d + \sum_\sigma H^c_\sigma + H^1_\sigma$.

$$H^c_\sigma = \sum_k \varepsilon_k c^\dagger_{k\sigma} c_{k\sigma} \qquad (5.2.2)$$

$$H^d = \sum_\sigma E_{d\sigma} n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} \qquad (5.2.3)$$

$$H'_\sigma = \sum_k V_{kd} c^\dagger_{k\sigma} c_{d\sigma} + h.c. \equiv V(\psi^\dagger_\sigma c_{d\sigma} + h.c.) \qquad (5.2.4)$$

The partition function expansion is

$$\frac{Z(H)}{Z(H^c)} = \left\langle Tr_d\, e^{-\beta H^d} T \exp -\int_0^1 H'_\uparrow(x)dx \exp -\int_0^1 H'_\downarrow(x')dx' \right\rangle_{\beta H^c}$$
$$= \sum_{mn}(-1)^{m+n}\int_0^1 dx_m \int_0^{x_m} dx_{m-1}\cdots\int_0^{x_2} dx_1 \int_0^1 dy_n \cdots \int_0^{y_2} dy_1 \left\langle Tr_d e^{-\beta H^d} T\, H'_\uparrow(x_m)\cdots H'_\uparrow(x_1)\, H'_\downarrow(y_n)\cdots H'_\downarrow(y_1)\right\rangle_{\beta H^c} \qquad (5.2.5)$$

Because H^d is not a free particle Hamiltonian, Wick's Theorem will only apply to H^c and expectation values of the operators $\psi, \psi^\dagger$. A basis of the exact eigenstates of H^d must be used. They are $|-\rangle = |vac\rangle$ $|\sigma\rangle = c^\dagger_{d\sigma}|vac\rangle$, and $|+\rangle = c^\dagger_{d\uparrow}c^\dagger_{d\downarrow}|vac\rangle$. H^d and H^1 may be written in terms of standard basis operators $X_{\alpha\beta} \equiv |\alpha\rangle\langle\beta|$:

$$H^d = \sum_\alpha E_\alpha X_{\alpha\alpha} \qquad (5.2.6)$$

$$H'_\sigma = \sum_{\alpha\beta} V^\sigma_{\alpha\beta} \psi^\dagger_\sigma X_{\alpha\beta} + h.c. \qquad (5.2.7)$$

where

$$X_{\alpha\beta}(x) = e^{x\beta(E_\alpha - E_\beta)} X_{\alpha\beta}. \qquad (5.2.8)$$

The conduction band propagators take a particularly simple form in the case $\Delta(\omega) = \Delta$:

$$V^2\langle T\psi(x)\psi^\dagger\rangle_{\beta H^c} = V^2\langle T\psi^\dagger(x)\psi\rangle_{\beta H^c}$$
$$= \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega\, \Delta(\omega)\cdot\frac{e^{x\beta\omega}}{1+e^{\beta\omega}} - \frac{e^{-x\beta\omega}}{1+e^{-\beta\omega}}$$
$$= \Delta/(\beta\sin\pi x) \qquad (5.2.9)$$

It is instructive to examine the expansion for the general form

$$H = \sum_\alpha \tilde{E}_\alpha X_{\alpha\alpha} + \sum_{\alpha\beta} \tilde{V}_{\alpha\beta} X_{\alpha\beta} \qquad (5.2.10)$$

The Anderson model may be written in this form, too. The partition function expansion is

$$Z = \sum_N (-\beta)^N \sum_{\alpha_1\cdots\alpha_N} \int_0^1 dx_N \int_0^{x_N} dx_{N-1}\cdots\int_0^{x_2} dx_1 \cdot \tilde{V}_{\alpha_1\alpha_N}\tilde{V}_{\alpha_N\alpha_{N-1}}\cdots\tilde{V}_{\alpha_2\alpha_1} \exp -\sum_\alpha \beta\tilde{E}_\alpha T_\alpha \qquad (5.2.11)$$

where T_α is the total 'interval' spent in state $|\alpha\rangle$. This expansion may be interpreted as a sum over all 'paths' or 'histories' on a circular path of unit length (Fig. (5.1)):

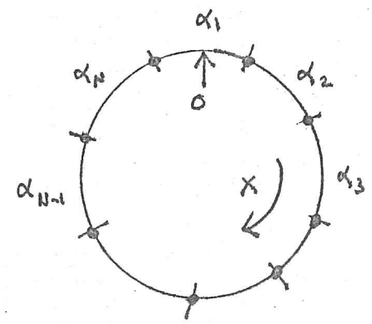


Fig. (5.1)
A 'history' or 'path' of the system governed by (5.2.10). (see text).

By integrating over the position of the origin, the expansion can be expressed as a sum over all distinct cyclical sequences $\alpha_1 \to \alpha_2 \to \cdots \to \alpha_N \to \alpha_1$. If $\mathcal{N}$ is the number of ways a sequence may be 'rotated' into itself:

$$Z = \int_{\text{distinct histories}} \frac{1}{\mathcal{N}} \left(\prod_i (-\beta\tilde{V}_{\alpha_i\alpha_{i+1}})\right) \exp -\sum_\alpha \beta\tilde{E}_\alpha T_\alpha \qquad (5.2.12)$$

In the Anderson model, $V_{\alpha\beta}$ is separable in subspaces of fixed fermion number: $V_{\alpha\beta} = \lambda v^*_\alpha v_\beta$ ($N^\alpha_\sigma = N^\beta_\sigma$). Only even cycles have non-zero amplitude, as an electron of a given spin must hop on and off the impurity orbital an equal number of times for the system to return to its original configuration. The product $\prod_i(-V_{\alpha_i\alpha_{i+1}})$ becomes $(-\lambda)^N \prod_i |v_{\alpha_i}|^2$ (N even), and all allowed 'histories' of the system have real positive amplitude.

This property simplifies the expansion for the Anderson model based on (5.2.6) and (5.2.7), as only the moduli of amplitudes need to be calculated.

Since they act in different subspaces, X and ψ operators either commute or anticommute:

$$\psi_\sigma^+(x)\, X_{\alpha\beta}(x') = \pm X_{\alpha\beta}(x')\, \psi_\sigma^+(x) \qquad (5.2.13)$$

$$\psi_\uparrow(x)\, \psi_\downarrow^+(x') = -\psi_\downarrow^+(x')\, \psi_\uparrow(x) \qquad (5.2.14)$$

As the overall sign of the amplitude is known to be positive, $\psi_\uparrow$, $\psi_\downarrow$, and X may be treated as commuting operators, and expectation values factorised into products of factors for each of the three independent subspaces.

Adapting (5.2.5) to the Anderson model, it is seen that:

(1) As $n_{d\sigma} = 0$ or 1 only, there must be an even number of events $x_1, \ldots x_{2M}$, $y_1 \ldots y_{2N}$, and if (say) x_{2i} represents emission of an $\uparrow$-spin fermion, x_{2j-1} represents absorbtion of one, or vice versa, depending on the initial state of the system at x=0.

(2) The trace over the initial state of the d-orbital at x=0 can be incorporated into the integration limits by extending the range of the integrals over x_1, y_1. The state of the impurity can be defined to be (say) $|->$ in the sector

$$\alpha = - \quad \text{for } x \text{ s.t. } \max(x_{2M}, y_{2N}) - 1 < x < \min(x_1, y_1)\ . \qquad (5.2.15)$$

The sum over the four initial states at x=0 can be carried out by choosing this convention and extending the range of the x_1 integration from $(0,x_2)$ to $(x_{2M}-1, x_2)$ and y_1 from $(0,y_2)$ to $(y_{2N}-1, y_2)$.

The choice (5.2.15) means that x_i, y_i are emission events for i even and absorbtion events for i odd. With factorisation of expectation values, (5.2.5) - (5.2.7) become:

$$\frac{Z(H)}{Z(H_c)} = \sum_{mn} \int_0^1 d x_{2m} \cdots \int_{x_{2m-1}}^{x_2} d x_1 \int_0^1 d y_{2n} \cdots \int_{y_{2n-1}}^{y_1} d y_1 \, (\beta V)^{2(M+N)} \exp -\sum_\alpha E_\alpha T_\alpha(\{x_i, y_i\}) \cdot$$

$$(x_{2m} > x_{2m-1} > \cdots > x_1 > x_{2m-1})$$

$$\cdot \left| \langle T \psi^+(x_{2m}) \cdots \psi(x_1) \rangle_{H_c} \right| \cdot \left| \langle T \psi^+(y_{2n}) \cdots \psi(y_1) \rangle_{H_c} \right| \qquad (5.2.16)$$

where

$$(T_- + T_\downarrow) = \sum_i (-1)^i x_i \ ; \quad (T_- + T_\uparrow) = \sum_i (-1)^i y_i \ ;$$

$$T_+ = -\frac{1}{2} \sum_{i>j} (-1)^{i-j} |x_i - y_j| \ ; \quad T_- + T_\uparrow + T_\downarrow + T_+ = 1 \qquad (5.2.17)$$

Using Wick's theorem and (5.2.9) on the conduction band expectation values, and a shorthand notation for the integrations in (5.2.16):

$$\frac{Z(H)}{Z(H_c)} = \sum_{mn} \left(\prod \int dx \int dy \right) (\beta\Delta)^{m+n} \exp -\sum_\alpha \beta E_\alpha T_\alpha \cdot$$

$$\cdot \left| \det_{ij} \frac{1}{\sin \pi (x_{2i} - x_{2j-1})} \right| \cdot \left| \det_{ij} \frac{1}{\sin \pi (y_{2i} - y_{2j-1})} \right| \qquad (5.2.18)$$

These determinants may be evaluated as they can be put into Cauchy form (Polya and Szegö (1945)):

$$\det_{ij} \frac{1}{\sin(a_i - b_j)} = \frac{\prod_{i>j} \sin(a_i - a_j) \sin(b_j - b_i)}{\prod_{ij} \sin(a_i - b_j)} \qquad (5.2.19)$$

Also, by inspection, since each permutation in the determinant changes the sign of the product, cancelling the sign change of the permutation:

$$\left| \det_{ij} \frac{1}{\sin(a_i - b_j)} \right| = \operatorname*{perm}_{ij} \frac{1}{\sin |a_i - b_j|} \qquad (5.2.20)$$

where 'perm.' indicates the permanent (analogous to the determinant, but without the factor for the sign of the permutation).

Two useful final forms of the partition function expansion are obtained:

$$\frac{Z(H)}{Z(H^c)} = \sum_{mn} \left(\pi \int dx \int dy\right) (\beta\Delta)^{m+n} \exp - \sum_\alpha \beta E_\alpha T_\alpha \cdot$$

$$\cdot \underset{ij}{\text{perm}} \frac{1}{\sin\pi|x_{2i}-x_{2j-1}|} \cdot \underset{ij}{\text{perm}} \frac{1}{\sin\pi|y_{2i}-y_{2j-1}|} \qquad (5.2.21)$$

and

$$\frac{Z(H)}{Z(H^c)} = \sum_{mn} \left(\pi \int dx \int dy\right) (\beta\Delta)^{m+n} \exp - \sum_\alpha \beta E_\alpha T_\alpha \cdot$$

$$\cdot \exp\left[\sum_{i>j} (-1)^{i-j} \left(\ln \sin\pi|x_i-x_j| + \ln \sin\pi|y_i-y_j|\right)\right] \qquad (5.2.22)$$

These surprisingly simple forms are exact. The form (5.2.22) is very similar to the Anderson and Yuval (1969) expansion for the Kondo model partition function, except that there the bandwidth is an essential parameter that must be kept finite. This requires the logarithms to have a cutoff for small argument, and in contrast to (5.2.22), the Anderson-Yuval form is only an 'asymptotically exact' approximate form for the Kondo model partition function.

5.3 Low Order Perturbation Theory for the Susceptibility of the Anderson Model

It is interesting to use this expansion to re-evaluate low order perturbation theory for the impurity susceptibility of the Anderson model. The expansion for the impurity susceptibility of the Kondo model is given by (2.4.2), repeated here.

$$\chi = \frac{1}{4kT}\left(1 + (J\rho) + (J\rho)^2 \ln(T/D) + \cdots\right) \qquad (5.3.1)$$

where $D = (D_1 D_2)^{\frac{1}{2}}$, and D_1, D_2 are cutoffs or the upper and lower effective band edges. Scalapino (1966) and subsequent workers (Keiter and Kimball (1971)) report this form for the impurity susceptibility of the Anderson model, and find $J\rho$ as given by the Schrieffer-Wolff transformation $\left(\frac{2\Delta}{\pi}\left(\frac{1}{E_j} - \frac{1}{E_j+U}\right)\right)$, but identify the Kondo bandwidth parameter D with the Anderson model bandwidth W. In the light of the discussion in 5.1, this is clearly incorrect in the $W \to \infty$ limit; the numerical renormalisation group study by Krishna-Murthy et al. (1975) reported correspondence to the Kondo problem with $D \simeq U/12$ independent of W (for W>>U), for the symmetric case. These earlier authors worked in a formalism using energy variables, which loses the simplicity of the expansion in 'imaginary time' variables, and calculated only 'dominant diagrams.' They clearly have omitted those diagrams that cancel the dependence on W.

For low order calculations, it is best to explicitly retain conduction electron propagators and work with the form (5.2.21). Integrating out the position of the origin x=0, the partition function is given by:

$$Z = \int_{\substack{\text{distinct} \\ \text{diagrams}}} \frac{1}{N} \exp - \sum_\alpha \beta E_\alpha T_\alpha \times \prod \frac{\beta\Delta}{\sin\pi|x_i-x_j|} \qquad (5.3.2)$$

with a factor for each conduction band particle or hole line. Writing

$\beta E_\sigma = \frac{1}{2}\beta H\sigma = \frac{1}{2}h\sigma$ $(\sigma = \pm 1)$, $\beta E_+ = \beta(E_d+U) = \varepsilon_+$, $\beta E_- = -\beta E_d = \varepsilon_-$, and representing states $|+\rangle$, $|-\rangle$ by $|\tau\rangle$, $\tau = \pm 1$, the expansion is diagrammatically given in Fig. (5.1):

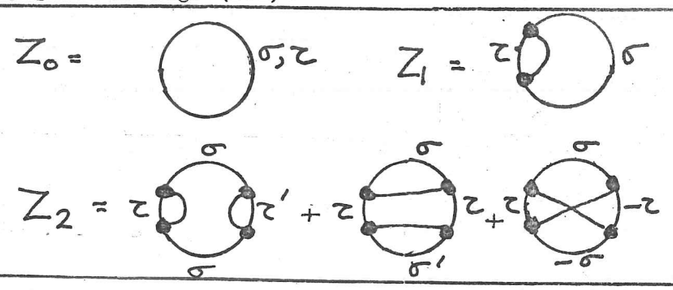


Fig. (5.1)

Partition function expansion for the Anderson model.

The relation to a equivalent expansion for the Kondo model, in the $\varepsilon^+, \varepsilon^- >> 1$ limit, is apparent (Fig. (5.2)); the average length of the intervals spent in states $\tau = +,-$ become very small, as these states are energetically unfavorable, and may be incorporated into a new vertex.

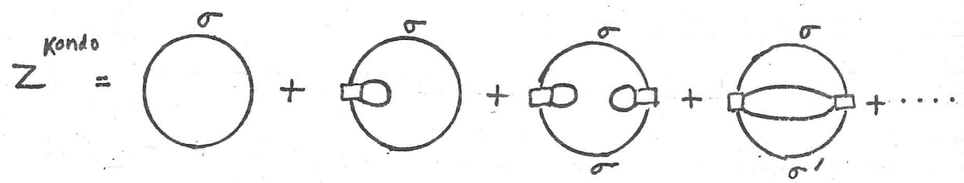


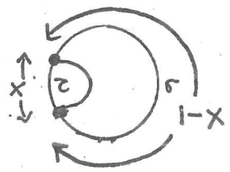
Fig.(5.2) Kondo model expansion as a limit of Fig.(5.1)

The translation of the diagrammatic series of Fig. (5.1) proceeds as follows:

Zeroth order:

$$Z_0 = \exp-\varepsilon^- + \exp-\varepsilon^+ + \exp-h/2 + \exp+h/2$$
$$= \exp-\varepsilon^- + \exp-\varepsilon^+ + 2\cosh h/2 \quad . \qquad (5.3.3)$$

First order: there is only one diagram to consider; use the integration variable x:



The first order term is then

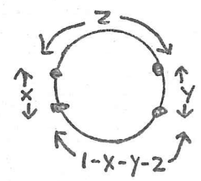
$$Z_1 = (\beta\Delta)\int_0^1 \frac{dx}{\sin\pi x}\left(\exp-\varepsilon^- x + \exp-\varepsilon^+ x\right)\cdot\left(2\cosh h/2(1-x)\right) \qquad (5.3.4)$$

where there is a factor $(\beta\Delta)/\sin(\pi x)$ associated with the conduction electron propagator, factors $\exp-\varepsilon_\tau x$ associated with the interval x spent in states $\tau = +,-$, and factors $\exp-\frac{1}{2}h\sigma(1-x)$ associated with the interval $(1-x)$ spent in states $\sigma = \uparrow, \downarrow$. The possible values of σ, τ are then summed over. The singularities of the factor $1/\sin(\pi x)$ should be regularised in the following way:

$$\frac{1}{\sin\pi x} = \lim_{\epsilon\to 0^+} \frac{\theta(x-\epsilon)\,\theta(1-x-\epsilon)}{\sin(\pi x)} \quad . \qquad (5.3.5)$$

ϵ is essentially a bandwidth cutoff; though the expansion for Z is term by term divergent in the limit $\epsilon\to 0$, expansions for derivatives of the free energy that may be derived from it are well-behaved, as pointed out in section (5.1).

Second order: integration variables used will be x,y, and z:



Clearly the integration volume is restricted by $x \geq 0$, $y \geq 0$, $z \geq 0$, $1-x-y-z \geq 0$. Furthermore, because of the two intervals z and 1-x-y-z spent in states σ , double counting of equivalent diagrams must be avoided by restricting integration to $z \leq 1-x-y-z$, i.e, $1-x-y-2z \geq 0$. Applying the rules used in the first order case to the three second order diagrams:

$$Z_2 = (\beta\Delta)^2 \int_0^1 dx \int_0^1 dy \int_0^{1/2} dz \;\; \Theta(1-x-y-2z) \cdot$$

$$\left(\frac{\exp-\varepsilon^- x + \exp-\varepsilon^+ x}{\sin \pi x}\right)\left(\frac{\exp-\varepsilon^+ y + \exp-\varepsilon^- y}{\sin \pi y}\right)\left(2\cosh \frac{h}{2}(1-x-y)\right)$$

$$+ \left(\frac{\exp-\varepsilon^-(x+y) + \exp-\varepsilon^+(x+y)}{\sin \pi z \;\; \sin \pi(x+y+z)}\right)\left(2\cosh \frac{h}{2}(1-x-y) + 2\cosh \frac{h}{2}(1-x-y-2z)\right)$$

$$+ \left(\frac{\exp-\varepsilon^- x \exp-\varepsilon^+ y + \exp-\varepsilon^+ x \exp-\varepsilon^- y}{\sin \pi(z+x) \;\; \sin \pi(z+y)}\right)\left(2\cosh \frac{h}{2}(1-x-y-2z)\right) \qquad (5.3.6)$$

Higher order terms may be constructed, but of course become progressively more complicated.

For calculation of impurity properties, the infinite bandwidth Anderson model used here is expecially convenient. This is because there is no conduction electron polarisation (this is Anderson's (1961) so-called "compensation theorem"); the change in the conduction electron density of states caused by the impurity is

$$\delta\rho_{cond.}(\omega) = \frac{1}{\pi} \mathrm{Im}\left(\frac{d}{d\omega}\left(\Sigma_{sd}(\omega)\, G_d(\omega)\right)\right) \qquad (5.3.7)$$

which vanishes because

$$\frac{d}{d\omega}\Sigma_{sd}(\omega) = \frac{d}{d\omega}\int_{-\omega}^{\omega} \frac{\Delta}{\omega - x}\, dx = 0 \qquad (5.3.8)$$

The <u>total</u> impurity susceptibility can then simply be obtained by finding the reponse to the <u>local</u> field H, which couples only to the impurity d-orbital.

This is easily obtained by taking the second derivative of the partition function with respect to h:

$$\chi^{imp} = \chi_{dd} = \beta Z^{-1} \frac{d^2 Z}{dh^2}\bigg)_0 \equiv \beta \frac{Z''}{Z} \qquad (5.3.9)$$

If the expansion for Z in powers of Δ is $Z_0 + Z_1 + Z_2 \ldots\ldots$, the expansion for χ is

$$\chi = \frac{\beta Z_0''}{Z_1}\left(1 + \left(\frac{Z_1''}{Z_0''} - \frac{Z_1}{Z_0}\right) + \left[\left(\frac{Z_2''}{Z_0''} - \frac{Z_2}{Z_0}\right) - \frac{Z_1}{Z_0}\left(\frac{Z_1''}{Z_0''} - \frac{Z_1}{Z_0}\right)\right] \ldots\right) . \qquad (5.3.10)$$

These terms may be constucted using (5.3.3), (5.3.4) and (5.3.9). This is done in appendix 5A, where these combinations of terms are explicitly demonstrated to be well-behaved in the $\epsilon \to 0$ (infinite bandwith) limit of the partition function expansion. The susceptibility expansion is also evaluated in various asymptotic limits of $\varepsilon^+, \varepsilon^-$ large and small.

In the <u>high temperature</u> ($|\varepsilon^+|, |\varepsilon^-| \ll 1$) limit (appendix 5A- section (II), Eqn.(5.A.29)) χ is given by:

$$\chi = \frac{1}{8T} + \frac{1}{32T^2}\left(U - \frac{8A\Delta}{\pi}\right) + O\left(\frac{1}{T^3}\right) \quad (|E_d|, U < T) \qquad (5.3.11)$$

The Curie law factor of 1/8 reflects the effective fourfold degeneracy of the impurity orbital at high temperatures. The integral A (which must be evaluated numerically) is associated with the broadening due to hybridisation of a d-level whose distance from the Fermi level is small compared to the temperature, and is given by:

$$A \equiv 2\pi \int_0^{1/2} \frac{dx}{\sin \pi x} \cdot x(1-x) = 0.85255\ldots \qquad (5.3.12)$$

For strong coupling, ($U \gg \Delta$) the effective "Curie constant" $T\chi$ <u>increases</u> above 1/8 as the temperature decreases; for weak coupling, it <u>decreases</u>.

In the intermediate temperature asymmetric limit $U \gg T \gg |E_d|$ or $\varepsilon^+ \gg 1$, $|\varepsilon^-| \ll 1$ (Appendix 5A - section (III), eqn. (5.A.38):

$$\chi = \frac{1}{6T}\left(1 - \frac{2\Delta}{\pi U} + O\left(\frac{\Delta^2}{U^2}\right)\right) - \frac{1}{18T^2}\left[\left(E_d - \frac{\Delta}{\pi}\ln\frac{T}{\alpha U}\right) + 3A\frac{\Delta}{\pi}\right] + O\left[\frac{(E_d,\Delta)^2}{T^3}\right]$$

$$+ \left(\frac{\Delta}{6\pi U^2} + O\left(\frac{\Delta^2}{U^3}\right)\right) + O\left(\frac{\Delta T}{U^3}\right). \qquad (|E_d| \ll T \ll U) \qquad (5.3.13)$$

where the coefficient α in the logarithmic term is

$$\alpha = \frac{2}{\pi}\exp C \quad , \quad (C = \text{Eulers Constant}, 0.577\ldots) \qquad (5.3.14)$$

In this large U limit, the leading term in the Curie constant rises to 1/6, reflecting the effective threefold degeneracy of the impurity. Fluctuations to the state $n_d = 2$ are effectively frozen out at these temperatures; the residual effect of such fluctuations are seen in the correction to the Curie constant, which is slightly less than 1/6, and the Pauli term $\sim \Delta/U^2$, which represents the small additional density of states available at the Fermi surface due to the tails of a quasi-lorentzian high-energy resonance with width Δ at an energy of order U. These terms vanish in the limit $U \to \infty$; however there is additional U-dependence in the logarithmic term $(\Delta/6\pi T^2)\ln(T/\alpha U)$ which diverges in that limit. This is because in an Anderson model with $U = \infty$ there is no longer any cancellation of ultra-high energy processes, and a finite bandwidth parameter is required. Using the terminology "asymmetric Anderson model" for such a $U = \infty$ model, the asymmetric Anderson model bandwidth parameter W may be defined by the perturbation expansion in Δ for χ equivalent to (5.3.13). In the temperature range $U \gg T \gg |E_d|$, the full strong-coupling ($U \gg \Delta$) Anderson model becomes equivalent to an asymmetric model with $W = \alpha U$, where α is given by (5.3.14). It might be considered that the term $3A\Delta/\pi T^2$ should be absorbed into the definition of W, since it is of the same form as $\Delta \ln \alpha/\pi T^2$; however, the term A is in fact associated with the broadening of the level near the Fermi surface,

and can be distinguished from the terms proportional to $\ln \alpha$ by examining the next level of terms, proportional to $1/T^3$, where these two type of contribution have a different E_d-dependence. The perturbation expansion in Δ for the susceptibility of the asymmetric Anderson model thus defines W by:

$$\chi = \frac{1}{6T} - \frac{1}{18T^2}\left[E_d - \left(\frac{\Delta}{\pi}\ln\frac{T}{W}\right) + 3A\frac{\Delta}{\pi}\right]$$

$$\cdot \frac{-1}{108T^3}\left[E_d^2 - 2E_d\left(\frac{\Delta}{\pi}\ln\frac{T}{W}\right) - 15A\frac{\Delta}{\pi}E_d + O(\Delta^2)\right]\cdots \qquad (5.3.15)$$

It is evident that absorbing the term involving A in the $1/T^2$ term into the definition of W would still leave terms involving A floating around unabsorbed in the $1/T^3$ term. (The $1/T^3$ term of (5.3.15) may be obtained from (5.A.38a) in appendix 5A). Higher order terms might define a series expansion $W(\Delta)$ in powers of Δ so that partially summing the series so logarithmic terms appeared as $\ln(T/W(\Delta))$ left only universal (i.e., band-structure-independent) series coefficients such as A and other similar integrals appearing in higher order terms of the high-temperature series (5.3.11).

In the low temperature Kondo limit, where E_d is below the Fermi surface, and E_d+U is above the Fermi surface, so that E_d+U, $|E_d| \gg T$, the susceptibility may be written as

$$\chi(T) = \chi^{\text{Kondo}}(T) + \chi^{\text{Pauli}} + O(T). \qquad (5.3.16)$$

(Appendix 5A - section (IV), eqn.(5.A.60,61)). The leading terms give rise to a series of Kondo form (5.3.1), with

$$(J\rho)^{\text{eff}} = \frac{2\Delta}{\pi}\left(\frac{1}{E_d} - \frac{1}{E_d+u}\right); \quad D_{(0)}^{\text{eff}} = \bar{\alpha}\left(|E_d|(E_d+u)\right)^{1/2}$$

$$\left(\bar{\alpha} = \frac{1}{2\pi}\exp(C + 1/4)\right) \qquad (5.3.17)$$

The parameter $J\rho^{eff}$ agrees with the Schrieffer-Wolff value, and has previously previously been obtained by such a perturbation expansion (Scalapino,(1966)). The new value is that for D^{eff}, which has not previously been obtained peturbatively. It corresponds to $(D_1 D_2)^{\frac{1}{2}}$, where D_1 and D_2 are the natural upper and lower cutoffs (E_d+U) and $|E_d|$. The precise numerical proportionality coefficient is also obtained. These values correspond to a Kondo series with a T_K of

$$T_K = D(|J\rho|)^{\frac{1}{2}} \exp \frac{1}{J\rho}$$

$$= \bar{\alpha}\left(\frac{2\Delta}{\pi U}\right)^{\frac{1}{2}} \exp \frac{E_d(E_d+U)}{(2\Delta U/\pi)} \quad ; \quad \left(\bar{\alpha} = \frac{\exp(C+1/4)}{2\pi}\right). \qquad (5.3.18)$$

Comparison of this expression with some numerical renormalisation group results is shown in the following table:

	$-E_d/W$	U/W	$2\Delta/\pi W$	$-E_d/U$	$-J\rho^{eff}$	$(T_K/W)^{calc}$	T_K^{theo}/T_K^{calc}
a.	0·5 $\times 10^{-3}$	1·0 $\times 10^{-3}$	1·6 $\times 10^{-5}$	0·5	0·064	3·7 $\times 10^{-12}$	2·0
b.	1·0 $\times 10^{-5}$	1·0 $\times 10^{-3}$	1·0 $\times 10^{-6}$	10^{-2}	0·100	2·6 $\times 10^{-10}$	2·0
c.	1·0 $\times 10^{-5}$	1·0 $\times 10^{-2}$	1·0 $\times 10^{-6}$	10^{-3}	0·100	7·6 $\times 10^{-10}$	2·2

Source: (a) Krishna-murthy et al. (1975); (b),(c) Krishna-murthy H.R., private communication. (W is a bandwidth used in the numerical work). The numerical accuracy is said to be a few per cent.

The results range over a wide spread of asymmetry and represent bona-fide Kondo systems since $T_K \ll \Delta$. The ratio of the theoretical prediction from (5.3.18) to the numerical result is shown in the final column. There is perfect agreement between the functional form of (5.3.18) and the numerical calculation, but the theoretical value is systematically a factor of about two higher. This may be due to an error in calculating the numerical

prefactor of (5.3.18) from perturbation theory - tantalisingly, replacing the factor $\exp(C+\frac{1}{4})$ by $\exp(C-\frac{1}{2})$ would give essentially perfect agreement - however attempts to find such a correction have been fruitless despite much effort. Possible sources of a systematic error in the numerical calculations will be briefly discussed later.

The leading, Kondo terms in the susceptibility expansion may be identified with the spin fluctuations: depending on the single parameter T_K these terms, when summed, contain no memory of the levels E_d, E_d+U to which residual charge fluctuations are possible. These charge fluctuations contribute to the next leading terms, the Pauli susceptibility (5.A.61). The full term is complicated, and given in the appendix 5A; its form in two special limits will be given here - the symmetric case, $E_d=-\frac{1}{2}U$

$$\chi^{Pauli} = \frac{2\Delta}{\pi U^2}\left(1 - \frac{6\cdot\Delta}{\pi U} + O\left(\frac{\Delta}{U}\right)^2\right) \qquad (E_d = -U/2,) \qquad (5.3.19)$$

and the asymmetric limit, $U \gg -E_d \gg T$:

$$\chi^{Pauli} = \frac{\Delta}{4\pi E_d^2}\left(1 - \frac{2\Delta}{\pi E_d}\left(\ln\left|\frac{U}{E_d}\right| - \frac{1}{2}\right) + O\left(\frac{\Delta}{E_d}\right)^2 \ldots\right)$$

$$(U \gg -E_d \gg T) \qquad (5.3.20)$$

As in the intermediate $U \gg T \gg |E_d|$ regime, there is logarithmic dependence on U which plays the role of a cutoff.

In the other low temperature limit, the non-magnetic regime E_d+U, $E_d \gg T$ (Appendix 5A - section (V), eqn.(5.A.90)) the expansion is well behaved, and the leading terms are a Pauli susceptibility, given in full in the appendix, but quoted here in the asymmetric limit $U \gg E_d \gg T$:

$$\chi^{Pauli} = \frac{\Delta}{2\pi E_d^2}\left(1 - \frac{2\Delta}{\pi E_d}\left(\ln\left|\frac{U}{E_d}\right| - \frac{1}{2}\right) + O\left(\frac{\Delta}{E_d}\right)^2\right) \qquad (5.3.21)$$

$$(U \gg E_d \gg T)$$

Note how the correction factors of the two Pauli susceptibilities (5.3.20) and (5.3.21) are the same. In the non-magnetic $E_d \gg T$ limit the full susceptibility is given by

$$\chi(T) = \chi^{Pauli} + O(T) \qquad (5.3.22)$$

Because it generates its own cutoff in such a natural way, the Kondo limit of the Anderson model could provide a very suitable case for a perturbation-theoretic test of the 'universality' of the weak coupling Kondo problem. The statement of universality is equivalent to the assertion that a universal Kondo temperature T_K exists (Wilson (1975)) such that

$$T_K = D(J\rho) \exp -\Phi(J\rho) \qquad (5.3.23)$$

$$D(J\rho) = D + D' J\rho + \tfrac{1}{2}D''(J\rho)^2 + \cdots \qquad (5.3.24)$$

where $D(J\rho)$ is a non-universal power series that depends on the details of the particular band structure, and $\Phi(x)$ is a universal function with the expansion

$$\Phi(x) = -\frac{1}{x} - \tfrac{1}{2}\ln|x| + \left(\tfrac{1}{4} + \tfrac{4}{3}a\right)x + O(x^2) \qquad (5.3.25)$$

(note that this follows the convention of Krishna-murthy et al. (1975); as Wilson (1975) defines it, the RHS of (5.3.25) is '$\Phi(\frac{1}{2}x)$'). Wilson reports the coefficient of x in (5.3.25) as $\frac{1}{2}$X3.1648±0.01%, or a = 0.9993 ± 0.0001. The universal susceptibility $\chi(T)$ is obtained from Φ:

$$\Phi(4T\chi(T) - 1) = \Phi(J\rho) + \ln(T/D(J\rho)) \qquad (5.3.26)$$

(cf. (2.4.11). Expanding Φ, and rearranging,

$$\chi(T) = \frac{1}{4T}\left(1 + J\rho + (J\rho)^2 \ln(T/D(J\rho)) + (J\rho)^3\left[\ln^2(T/D(J\rho)) + \tfrac{1}{2}\ln(T/D(J\rho))\right] + (J\rho)^4\left[\ln^3(T/D(J\rho)) + \tfrac{5}{4}\ln^2(T/D(J\rho)) - \tfrac{4}{3}a\ln(T/D(J\rho))\right] + \cdots\right) \qquad (5.3.27)$$

It seems likely that Wilson has underestimated the error in his calculation of a, and that it is precisely unity. This series (5.3.27)

is also universal, with $D(J\rho)$ containing all the band structure dependence. Expanding $D(J\rho)$ to obtain the full series in $(J\rho)$:

$$\chi(T) = \frac{1}{4T}\left(1 + J\rho + (J\rho)^2\ln(T/D) + (J\rho)^3\left[\ln^2(T/D) + \tfrac{1}{2}\ln(T/D) - \frac{D'}{D}\right] + (J\rho)^4\left[\ln^3(T/D) + \tfrac{5}{4}\ln^2(T/D) + \left(\tfrac{4}{3}a - 2\tfrac{D'}{D}\right)\ln(T/D) + \tfrac{1}{2}\left(\left(\frac{D'}{D}\right)^2 - \frac{D'}{D} - \frac{D''}{D}\right)\right] + \cdots\right) \qquad (5.3.28)$$

Evaluation of the power series of $D(J\rho)$ up to $(J\rho)^n$ requires perturbation theory to order n+2. It can be seen that evaluation of the expansion for χ to fourth order (i.e., eighth order in the Anderson model) would not only yield D' and D'', but, through the term in $(J\rho)^4\ln(T/D)$, provide a consistency test of universality, and the exact value of a. However, although this program is essentially straightforward, it has not been carried out as it involves a vast amount of algebra. Another aspect of the expansion (5.3.28) that is worth pointing out is that only the leading and next leading terms have explicitly universal coefficients (these are precisely the terms summed by the scaling equations to second order); the coefficients of the universal series (5.3.27) that emerges after partial summation of the full series (5.3.28) are hidden behind the non-universal derivatives of $D(J\rho)$ in all terms beyond the next leading ones of the full perturbation expansion (5.3.28).

The effect of retaining a finite bandwidth in the Anderson model may be taken into account by keeping the cutoff $\in$ of (5.3.5) finite, or introducing a similar cutoff to the logarithms in the alternative representation (5.2.22), namely the replacement

$$\ln(|x|/\tau) \to \ln^*(|x|/\tau) \simeq \begin{cases} \ln(|x|/\tau) & |x| > \tau \sim W^{-1} \\ 0 & |x| < \tau \sim W^{-1} \end{cases} \qquad (5.3.29)$$

This is only an approximation, but is asymptotically exact in the $\Delta/W \to 0$ limit. For $W \gg |E_d|, U$, the infinite bandwidth results will be

Note how the correction factors of the two Pauli susceptibilities (5.3.20) and (5.3.21) are the same. In the non-magnetic $E_d \gg T$ limit the full susceptibility is given by

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(cf. (2.4.11). Expanding Φ, and rearranging,

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is also universal, with $D(J\rho)$ containing all the band structure dependence. Expanding $D(J\rho)$ to obtain the full series in $(J\rho)$:

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The effect of retaining a finite bandwidth in the Anderson model may be taken into account by keeping the cutoff $\in$ of (5.3.5) finite, or introducing a similar cutoff to the logarithms in the alternative representation (5.2.22), namely the replacement

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This is only an approximation, but is asymptotically exact in the $\Delta/W \to 0$ limit. For $W \gg |E_d|$, U, the infinite bandwidth results will be

essentially unaffected; if W is smaller it will provide the cutoffs to any logarithmic terms that enter in perturbation theory. In particular, in the Kondo limit, the cutoffs D_1 and D_2 will be given by $\min(E_d+U,W)$ and $\min(-E_d,W)$. Thus, in the asymmetric Kondo limit, $U \gg |E_d|$, $-E_d \gg T$, the Kondo temperature is given by

$$T_K \sim (U\Delta)^{1/2} \exp \frac{\pi E_d}{2\Delta} \qquad (W \gg U \gg -E_d) \tag{5.3.30}$$

$$T_K \sim (W\Delta)^{1/2} \exp \frac{\pi E_d}{2\Delta} \qquad (U \gg W \gg -E_d) \tag{5.3.31}$$

$$T_K \sim W \left(\frac{\Delta}{|E_d|}\right)^{1/2} \exp \frac{\pi E_d}{2\Delta} \qquad (U \gg -E_d \gg W) \; . \tag{5.3.32}$$

5.4 Inclusion of Boson Terms in the Partition Functions

The exact result (5.2.22) may be extended to include screening terms, without making any approximations. If the level shifts due to the boson field relaxation are absorbed into the definitions of the E_α, (3.4.1) may be written

$$H^{scr} = \sum_\alpha X_{\alpha\alpha} H^b_\alpha \tag{5.4.1}$$

$$H^b_\alpha = \sum_q \omega_q (b^\dagger_q + g_\alpha \frac{\alpha_q}{\omega_q})(b_q + g_\alpha \frac{\alpha^*_q}{\omega_q}) \tag{5.4.2}$$

where

The operators $X_{\alpha\beta}(x)$ (5.2.8) now take the form

$$X_{\alpha\beta}(x) = e^{x\beta(E_\alpha - E_\beta)} X_{\alpha\beta} e^{x\beta H^b_\alpha} e^{-x\beta H^b_\beta} \tag{5.4.3}$$

The bosons contribute an extra factor to path amplitudes, of the form:

$$\langle T \exp -\beta \int_0^1 H^b(x) \rangle_{\beta H^b(0)} \tag{5.4.4}$$

where

$$H^b(x) = \sum_q \omega_q (b^\dagger_q + g n(x) \frac{\alpha_q}{\omega_q})(b_q + g n(x) \frac{\alpha^*_q}{\omega_q}) \tag{5.4.5}$$

$$n(x) = \sum_i \langle \alpha_i | n_d | \alpha_i \rangle \, \theta(x_{i+1} - x) \, \theta(x - x_i) \; . \tag{5.4.6}$$

The amplitude (5.4.4) is easily evaluated; define the boson operator $\phi = \sum_q \alpha_q b_q$;

In the interaction representation (5.4.4) becomes

$$\langle T \exp -\beta g \int_0^1 n(x)\phi(x)dx \; \exp -\beta g \int_0^1 n(x)\phi^\dagger(x)dx \rangle_{H^b(0)} \times$$

$$\exp -(\beta g)^2 \sum_q \frac{|\alpha_q|^2}{\omega_q} \int_0^1 n^2(x)dx \; . \tag{5.4.7}$$

Expanding the exponentials, and noting that only expectation values of products of equal numbers of boson creation and annihilation operators are non-vanishing,

$$\langle \cdot \rangle_{H^b(0)} = \sum_N \frac{(\beta g)^{2N}}{N!} \left(\prod_{i=1}^N \int_0^1 n(x_i)dx_i \int_0^1 n(y_i)dy_i \right) \langle T\phi(x_1)\cdots\phi(x_N)\phi^\dagger(y_1)\cdots\phi^\dagger(y_N)\rangle_{H^b(0)}$$

$$= \sum_N \frac{(\beta g)^{2N}}{N!} \prod_{i=1}^N \left(\int_0^1 n(x_i)dx_i \int_0^1 n(y_i)dy_i \langle T\phi(x_i)\phi^\dagger(y_i)\rangle_{H^b(0)} \right)$$

$$= \exp\left[(\beta g)^2 \int_0^1 n(x)dx \int_0^1 n(y)dy \langle T\phi(x)\phi^\dagger(y)\rangle_{H^b(0)} \right] \tag{5.4.8}$$

Using symmetry under interchange of x and y (5.4.8) becomes

$$\exp\left[\int_0^1 dx\, n(x) \int_0^1 dy\, n(y)\, f(x-y)\right] \qquad (5.4.9)$$

$$f(x-y) = (\beta g)^2 \left[\tfrac{1}{2}\left(\langle T\phi(x)\phi^\dagger(y)\rangle + \langle T\phi^\dagger(x)\phi(y)\rangle\right) - \sum_q \frac{|\alpha_q|^2}{\omega_q}\delta(x-y)\right]$$

$$= (\beta g)^2 \sum_q |\alpha_q|^2 \left(\tfrac{1}{2}\left(\frac{\exp\beta\omega_q|x-y|}{\exp\beta\omega_q - 1} + \frac{\exp-\beta\omega_q|x-y|}{1-\exp-\beta\omega_q}\right) - \frac{\delta(x-y)}{\omega_q}\right)$$

$$= \frac{\partial}{\partial x}\frac{\partial}{\partial y} F(|x-y|) \qquad (5.4.10)$$

where

$$F(x) = \frac{(\beta g)^2}{2}\sum_q \frac{|\alpha_q|^2}{\omega_q^2}\left(\frac{\exp x\beta\omega_q}{\exp\beta\omega_q - 1} + \frac{\exp -x\beta\omega_q}{1-\exp-\beta\omega_q}\right) + \text{constant.} \quad (0\le x\le 1) \qquad (5.4.11)$$

F(x) is undetermined by a constant, and F(x) = F(1-x).

Integrating (5.4.9) by parts, using (5.4.10), it becomes

$$\exp -\int_0^1 dx \int_0^1 dy\, n'(x)\, n'(y)\, F(|x-y|) \qquad (5.4.12)$$

Using (5.4.6), the final form for the boson factor is

$$\exp -\sum_{ij} \Delta n(x_i)\,\Delta n(x_j)\, F(|x_i - x_j|) \qquad (5.4.13)$$

where $\Delta n(x_i)$ is the change in $\langle n_d\rangle$ at x_i. The full (exact) expression for the partition function of the infinite bandwidth Anderson model with boson coupling is then

$$\frac{Z}{Z^0} = \sum_{mn} (\beta\Delta)^{m+n} \int_0^1 dx_{2m} \cdots \int_{x_{2m-1}}^{x_2} dx_1 \int_0^1 dy_n \cdots \int_{y_{2n-1}}^{y_2} dy_1 \cdot \exp -\{\cdot\}$$

$$\{\cdot\} = \Big\{\beta \sum_\alpha E_\alpha T_\alpha - \sum_{i>j} (-1)^{i-j}\left(\ln\sin\pi|x_i - x_j| + \ln\sin\pi|y_i - y_j|\right)$$
$$+ \sum_{ij}(-1)^{i-j}\left(F(|x_i - x_j|) + F(|y_i - y_j|) + 2F(|x_i - y_j|)\right)\Big\}.$$

$$\sum_\alpha E_\alpha T_\alpha = E_- + (E_\uparrow - E_-)\sum_i (-1)^i x_i + (E_\downarrow - E_-)\sum_j (-1)^j y_j - (E_\uparrow + E_- - E_\uparrow - E_\downarrow)\tfrac{1}{2}\sum_{ij}(-1)^{i-j}|x_i - y_j| \qquad (5.4.14)$$

It is interesting to note that this has the form of a configurational partition function of classical particles in a one-dimensional circular system, interacting only with pairwise forces, and external fields.

5.5 Specialisation to the Asymmetric Case.

To simplify matters, it is convenient to specialise to the asymmetric case, $U = \infty$, for the study of the mixed-valence problem. This removes $n_d = 2$ states from the problem, so attention can be focussed on fluctuations between the two configurational states $n_d = 0$ and $n_d = 1$. The only atomic states of the impurity orbital that contribute to the partition function are $|-\rangle$ (henceforth denoted as $|0\rangle$), $|\uparrow\rangle$ and $|\downarrow\rangle$.

As noted in section 5.3, taking the $U\to\infty$ limit necessitates retaining a finite conduction electron bandwidth W, to cut off logarithmic divergences in expansions for physical quantities. The necessary modification to (5.4.14) is

$$\ln(\sin\pi|x_i - x_j|) \longrightarrow \ln(\sin\pi|x_i - x_j|)\,;\ |x_i - x_j| \gg (\beta W)^{-1}$$
$$\longrightarrow \ln(\beta W)\,,\ |x_i - x_j| \ll (\beta W)^{-1} \qquad (5.5.1)$$

It is useful to define the function

$$\ln^*|x| = \ln|x|\ ;\ |x| \gg 1$$
$$= 0 \qquad |x| \ll 1 \qquad (5.5.2)$$

As mentioned at the end of section 5.4, the patition function may be interpreted as that of a gas; $\beta\Delta$ acts as a fugacity, and when $(\beta\Delta)\gg 1$, the mean separation between "particles" at x_i, x_j is of the order $(\beta\Delta)^{-1}$. The form (5.5.1) is exact except for $|x_i - x_j| \lesssim (\beta W)^{-1}$; configurations in which any of the "particles" are as close as $(\beta W)^{-1}$ contribute negligeably to teh partition function provided $(\beta W)^{-1}$ is much less than the average "inter-particle separation", i.e., if $W \gg \Delta$. At higher temperatures $(\beta\Delta) \ll 1$, the mean separation is of order unity, so the corresponding condition is $(\beta W)\gg 1$. The form (5.5.1) is thus asymptotically exact in the limit $W \gg \Delta, T$.

In this approximation, the partition function may be written:

$$\frac{Z}{Z_0} = \sum_N (\beta^2 W\Delta)^N \int_0^{'} dx_{2N} \cdots \int_{x_{2N-1}}^{x_2} dx_1 \sum_{\sigma_1 \cdots \sigma_{2N}} \prod_i \delta_{\sigma_{2i}\sigma_{2i-1}} \exp -\{\}$$

$$\{\} = \{ \sum_i (-1)^i E_{\sigma_i} x_i + \sum_{i>j} \delta_{\sigma_i\sigma_j} (-1)^{i-j} \ln^* (\beta W \sin\pi |x_i - x_j|)$$

$$+ \sum_{ij} (-1)^{i-j} F(|x_i - x_j|) \} \qquad (5.5.3)$$

x_{2i} represents emission of a particle with spin σ_{2i}; x_{2i-1} represents absorbtion of a particle with spin σ_{2i-1} ($= \sigma_{2i}$).

In the spirit of the asymptotic approximation , $F(x_i - x_j)$ may be replaced by its value for $|x_i - x_j| \gg (\beta W)^{-1}$, when $i \neq j$. Its behaviour for large argument depends on whether the bosons are phonons or Tomonagons.

In the case of phonons $F(x)$ behaves

$$F(x) = \frac{g^2}{2} \sum_q \frac{|\alpha_q|^2}{\omega_q^2} \cdot \coth\left(\frac{\beta\omega_D}{2}\right) \quad \text{for } |x| \ll (\beta\omega_D)^{-1}$$

$$F(x) \simeq 0 \quad \text{for } |x| \gg (\beta\omega_D)^{-1}. \qquad (5.5.4)$$

where ω_D is the Debye frequency. At high $T \gg \omega_D$ all pairs x_i, x_j are within the range of F, since $(\beta\omega_D)^{-1} \gg 1$; the sum in (5.5.3) becomes

$$\sum_{ij} (-1)^{i-j} F(|x_i - x_j|) = \sum_{ij} (-1)^{i-j} F(0) = 0 . \qquad (5.5.5)$$

The only effect of the phonons at temperatures above ω_D is thus the level shift that has been absorbed into E (this is a response to the mean diplacement of the boson field corresponding to each valence, a quantity which is independent of temperature when the electron-phonon coupling is linear, as in this model). However, in the other limit $\omega_D \gg T$ (and Δ), the mean separation $\overline{|x_i - x_j|}$ is much larger than $(\beta\omega_D)^{-1}$, and the

sum in (5.5.3) becomes

$$\sum_{ij} (-1)^{i-j} F(|x_i - x_j|) = \sum_i F(0) = 2N \frac{g^2}{2} \sum_q \frac{|\alpha_q|^2}{\omega_q^2}$$

$$(\omega_D \gg T, \Delta). \qquad (5.5.6)$$

This may be absorbed into Δ so that

$$\Delta \rightarrow \Delta \exp -g^2 \sum_q \frac{|\alpha_q|^2}{\omega_q^2} \equiv \Delta |\langle a|b\rangle|^2 \qquad (5.5.7)$$

The interpretation of this is very simple: when the characteristic fluctuation time (which is Δ^{-1} in the absence of phonons) is much larger than ω_D, the phonon field has ample time to fully relax about the impurity charge state in the interval between successive hops of an electron on and off the impurity orbital. The matrix elements V_{kd} are thus effectively reduced by the factor $\langle a | b \rangle$, the overlap between the coherent ground states of the phonon field appropriate to the two valence states; this was first pointed out in this context by Sherrington and Von Molnar (1975).

Thus the thermodynamics of the model at low temperatures is thus equivalent to that of a model without phonon coupling, but renormalised E_d and Δ .

The d-electron Greens function is

$$G_d(t) = -i \langle T C_d(t) C_d^+ \rangle_H \qquad (5.5.8)$$

This can be expanded in a similar fashion to the partition function. The only difference if that a term of order Δ^N now has 2(N+1) rather than 2N valence fluctuations in its amplitude, and there is a spare phonon overlap factor floating around, by which the Greens function must be multiplied. The correpondence of the model with phonon coupling to the one without (denoted by the suffix 0) is thus:

$$Z(E,\Delta) = Z^0(E',\alpha\Delta) \qquad (T,\Delta \ll \omega_D)$$

$$G_d(\omega,E,\Delta) = \alpha\, G^0_{Td}(\omega,E',\alpha\Delta) \quad (\omega,T,\Delta \ll \omega_D)$$

$$\alpha = \exp -g^2 \sum_q' \frac{|\alpha_q|^2}{\omega_q^2} \equiv |\langle a|b\rangle|^2 \qquad (5.5.9)$$

Note that there is a fundamental restriction on the magnitude of Im.G_d: writing G_d as $(\omega - E_d - \Sigma_{sd}(\omega) - \Sigma_{int}(\omega))^{-1}$. where Σ_{sd} is the self energy due to hybridisation with the conduction band (n.b. Im. $\Sigma_{sd} = \Delta$) and Σ_{int} is that due to interaction processes, it is easily seen that

$$Im\, G_d(\omega) \leq \frac{1}{Im(\Sigma_{sd} + \Sigma_{int})} \leq \frac{1}{\Delta} \qquad (5.5.10)$$

The form in (5.5.9) is seen to respect this limit:

$$Im\, G_d(\omega) = \alpha\, Im\, G^0_d(\omega) \leq \alpha \cdot \frac{1}{\alpha\Delta} = \frac{1}{\Delta} \qquad (5.5.11)$$

In the case of Tomonaga bosons, representing electronic screening processes, F(0) as defined by (5.4.11) is divergent. This is easily remedied, as F(x) is undetermined by an arbitrary constant, allowing the divergence to be subtracted:

$$F(x) = \frac{g^2}{2} \sum_q \frac{|\alpha_q|^2}{\omega_q^2} \left(\frac{\exp -x\beta\omega_q - 1}{\exp \beta\omega_q - 1} - \frac{1 - \exp -x\beta\omega_q}{1 - \exp -\beta\omega_q} \right) \qquad (5.5.12)$$

hence

$$F(0) = 0$$

$$F(x) = -\frac{\varepsilon}{2} \ln (\beta W \sin \pi x) \qquad x \gg (\beta W)^{-1} \qquad (5.5.12)$$

Here W is the high energy cutoff of the boson spectrum , which is just the bandwidth of the conduction electrons from which these bosons were derived; ε is just the exponent characterising the long-time screening response defined in (3.4.4). In asymptotic approximation,

$$F(x) = -\frac{\varepsilon}{2} \ln^*(\beta W \sin \pi |x|) \qquad (5.5.13)$$

and the exponential term in the partition function expansion (5.5.3) can be rewritten

$$\{\} = \left\{ \sum_i (-1)^i E_{\sigma_i} x_i - \sum_{i>j} (-1)^{i-j} (\gamma \delta_{\sigma_i\sigma_j} + \epsilon) \ln^*(\beta W \sin \pi |x_i - x_j|) \right\} \qquad (5.5.14)$$

where $\gamma = 1$.

It should be noted that such a form for the partition function could have been obtained directly from the model with an electronic screening term without going through the intermediate Tomonaga boson representation. Such a direct treatment would use the techniques developed by Nozieres and deDominicis (1968) to solve the X-ray edge problem, and applied by Anderson and Yuval (1969) to the Kondo problem. This allows the identification of ϵ with the Nozieres-deDominicis X-ray exponent; it also allows the type of screening potential considered here to be generalised to include screening in the same channel as the d-electron, and allows ϵ to become negative if this is important- an effect that cannot be handled within the framework of the Tomonaga boson representation used here.

For a spherically symmetric potential, ϵ is thus identified as

$$\epsilon = 2 \sum_L (2L+1) \left(\frac{\delta_L}{\pi}\right)^2 - 2\frac{\delta_{L_0}}{\pi} \qquad (5.5.15)$$

where the phase shifts δ_L satisfy the Friedel sum rule

$$2 \sum_L (2L+1) \left(\frac{\delta_L}{\pi}\right) = -1 \qquad (5.5.16)$$

and δ_{L_0} is the phase shift in the channel to which the d-electrons belong.

5.6 Equivalence to a Classical Spin Problem

Just as in the case of the Anderson-Yuval Kondo model partition function expansion (Yuval and Anderson (1970), the partition function (5.5. 2) may be interpreted as the partition function of a classical spin system on a circular one-dimensional lattice. Consider the model with Ising-like spins $S_i = -1,0,1$: $(S_{N+1} \equiv S_1)$

$$\mathcal{H} = E\sum_{i=1}^{N} S_i^2 + H\sum_i S_i - J\sum_i S_i S_{i+1} + K_1 \sum_{i>j} \frac{S_i S_j}{d_{ij}^2} + K_2 \sum_{i>j} \frac{S_i^2 S_j^2}{d_{ij}^2} \qquad (5.6.1)$$

where d_{ij} is the direct (chord) distance between sites i,j and N is large:

$$d_{ij} = \frac{N}{\pi} \sin \pi \frac{|i-j|}{N} \qquad (5.6.2)$$

For large positive (ferromagnetic) J, the lowest energy configuration will have S_i constant. Noting that

$$\sum_{i>j} \frac{1}{d_{ij}^2} = N \sum_{i=1}^{\infty} \frac{1}{i^2} + \frac{\pi^2}{N}\left(\sum_{i=1}^{N/2} \frac{1}{\sin^2 \frac{\pi i}{N}} - \sum_{i=1}^{\infty} \frac{1}{(\frac{\pi i}{N})^2}\right)$$
$$= N\frac{\pi^2}{6} + \pi \lim_{\varepsilon \to 0}\left(\int_{\varepsilon}^{\pi/2} \frac{dx}{\sin^2 x} - \int_{\varepsilon}^{\infty} \frac{dx}{x^2}\right) + O(\tfrac{1}{N})$$
$$= N\frac{\pi^2}{6} + O(\tfrac{1}{N}) \qquad (5.6.2)$$

the ground state configuration energy is

$$\mathcal{E}_0 = N\left(\left(E + \frac{\pi^2}{6}(K_1+K_2)\right)S^2 + HS\right) + O(\tfrac{1}{N});\ (S_i = S) \qquad (5.6.3)$$

For $(E+\frac{\pi^2}{6}(K_1+K_2))$ and H small (in a sense to be determined later), the dominant low energy configurations will be ones with S_i= constant over large segments; with a few widely separated discontinuities where the spin S_i changes (Fig. (5.3):

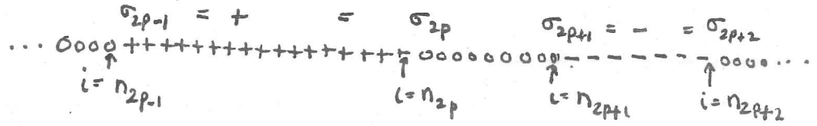

Fig. (5.3): Segment of a low energy configuration.

If the configuration has $S_i = \sigma_{2p}$ for $n_{2p-1} < i \le n_{2p}$, where $\sigma_{2p-1} = \sigma_{2p}$, $(\sigma_n = \pm 1)$, and $S_i = 0$ for $n_{2p} < i \le n_{2p+1}$, and $p = 1,\ldots 2m$, the configurational energy is:

$$\mathcal{H}\left(\{n_p, \sigma_p\}, p=1\cdots 2m\right) = 2mJ + E\sum_{p=1}^{2m}(-1)^p n_p + H\sum_p (-1)^p \sigma_p n_p$$
$$+ (K_1+K_2)\sum_p \sum_{i=n_{2p-1}+2}^{n_{2p}} \sum_{j=n_{2p-1}+1}^{i-1} \frac{1}{d_{ij}^2} + \sum_{p>q}(K_1\sigma_p\sigma_q + K_2)\sum_{i=n_{2p-1}+1}^{n_{2p}} \sum_{j=n_{2q-1}+1}^{n_{2q}} \frac{1}{d_{ij}^2} \qquad (5.6.5)$$

These sums can be evaluated:

$$\sum_{i=a+2}^{b} \sum_{j=a+1}^{i-1} \frac{1}{d_{ij}^2} = \sum_{i=a+2}^{b} \sum_{j=a+1}^{i-1} \frac{1}{|i-j|^2} + \frac{\pi^2}{N^2} \sum_{i=a+2}^{b} \sum_{j=a+1}^{i-1} \frac{1}{\sin^2 \frac{\pi}{N}(i-j)} - \frac{1}{(\frac{\pi}{N}(i-j))^2}$$
$(b \gg a)$
$$= \sum_{i=1}^{b-a-1} \frac{(b-a-i)}{i^2} + \int_{\frac{\pi a}{N}}^{\frac{\pi b}{N}} dx \int_{\frac{\pi a}{N}}^{x} dy \frac{1}{\sin^2(x-y)} - \frac{1}{(x-y)^2} + O(\tfrac{1}{N})$$
$$= (b-a)\frac{\pi^2}{6} - C - \ln(d_{ba}) + O(\tfrac{1}{N}) \qquad (5.6.6)$$

$$\sum_{i=c+1}^{d} \sum_{j=a+1}^{b} \frac{1}{d_{ij}^2} = \int_{\frac{\pi c}{N}}^{\frac{\pi d}{N}} dx \int_{\frac{\pi a}{N}}^{\frac{\pi b}{N}} dx \frac{1}{\sin^2(x-y)} + O(\tfrac{1}{N}) = \ln\left(\frac{d_{bd}\, d_{ac}}{d_{bc} d_{ad}}\right) + O(\tfrac{1}{N}) \qquad (5.6.7)$$
$(d \gg c \gg b \gg a)$

C is Eulers constant. Finally the Hamiltonian can be re-expressed as:

$$\mathcal{H}\left(\{n_p, \sigma_p\}, p=1\cdots 2m\right) = \mathcal{E}_0 + 2m\left(J - C(K_1+K_2)\right) + \left(E + \frac{\pi^2}{6}(K_1+K_2)\right)\sum_{p=1}^{M}(-1)^p n_p$$
$$+ H\sum_{p=1}^{M}(-1)^p \sigma_p n_p + \sum_{p>q}\left(K_1\sigma_p\sigma_q + K_2\right)(-1)^{p-q} \ln d_{n_p n_q}. \qquad (5.6.8)$$

The partition function is:

$$Z = e^{-\frac{\mathcal{E}_0}{T}}\left(1 + \sum_{M=1}^{\infty}\left[e^{\frac{C(K_1+K_2)-J}{T}}\right]^{2M} \sum_{\substack{n_{2M}=2M}}^{N} \sum_{n_{2M-1}=2M-1}^{n_{2M}-1} \cdots \sum_{n_2=2}^{n_3-1} \sum_{n_1=}^{n_2-1} \cdot \prod_{i=1}^{m} \delta_{\sigma_{n_{2i}}\sigma_{n_{2i-1}}} \exp -\{\cdot\}\right)$$

$$\{\cdot\} = +\sum_{p=1}^{2m}\left[\left(\frac{E}{T} + \frac{\pi^2}{6}\frac{(K_1+K_2)}{T}\right) + \sigma_p \frac{H}{T}\right](-1)^p n_p + \sum_{p>q}\left(\frac{K_1\sigma_p\sigma_q + K_2}{T}\right)(-1)^{p-q} \ln\left(d_{n_p n_q}\right) \qquad (5.6.9)$$

In the large N limit the sums over n_p can be replaced by integrals; the discreteness of the lattice provides the cutoff to the logarithms, and a partition function of the form (5.5.3) is recovered, with the identifications:

$$\begin{aligned}
\frac{\Delta}{W} &\longleftrightarrow \exp \frac{C(K_1+K_2)-J}{T} \\
\frac{E_\sigma}{W} &\longleftrightarrow \frac{E + \frac{\pi^2}{6}(K_1+K_2) + \sigma H}{T} \\
\beta W &\longleftrightarrow N \\
\gamma &\longleftrightarrow 2K_1/T \\
\epsilon &\longleftrightarrow \frac{K_2-K_1}{T}
\end{aligned} \tag{5.6.10}$$

The equivalence is for Anderson model parameters $\beta W \gg \beta\Delta \gg 1$: this is essentially an equivalence between the $\beta \to \infty$ limit of the weak-hybridisation Anderson model and the $N \to \infty$ or thermodynamic limit of the strongly ferromagnetic Ising chain. Subsidiary conditions are $E_\sigma \ll W$, and $K_1 \sim K_2 \sim 2T$.

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Appendix 5A. Perturbation expansion for the Anderson model susceptibility to second order in Δ ; asymptotic evaluation in various limits.

(I). Explicit demonstration of convergence in the infinite bandwidth limit.

The systematic expansion in powers of Δ for the partition function is given in (5.3.3-6); the expansion for the impurity susceptibility is related to it by (5.3.10):

$$\chi = \beta \frac{Z_0''}{Z_0}\left(1 + \left(\frac{Z_1''}{Z_0''} - \frac{Z_1}{Z_0}\right) + \left[\left(\frac{Z_2''}{Z_0''} - \frac{Z_2}{Z_0}\right) - \frac{Z_1}{Z_0}\left(\frac{Z_1''}{Z_0''} - \frac{Z_1}{Z_0}\right)\right] \cdots\right). \quad (5.A.1)$$

where $Z = Z_0 + Z_1 + Z_2 \cdots$, $Z'' = d^2Z/dh^2$. The prefactor $\beta\, Z_0''/Z_0$ is

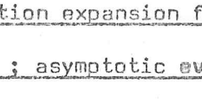
$$\beta \frac{Z_0''}{Z_0} = \frac{\beta}{4} \frac{2}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}} , \quad (5.A.2)$$

where $\varepsilon^+ = \beta(E_d+U)$, $\varepsilon^- = -\beta E_d$.

The first order term is given explicitly by

$$\frac{Z_1''}{Z_0''} - \frac{Z_1}{Z_0} = (\beta\Delta)\int_0^1 \frac{dx}{\sin\pi x}\left(\exp -\varepsilon^- x + \exp -\varepsilon^+ x\right)\left((1-x)^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right). \quad (5.A.3)$$

where the expression for Z_1 has been constructed, using the rules explained in section 5.3, from the diagrammatic representation:

$Z_1 =$  $, (\sigma = \uparrow, \downarrow \; ; \; \tau = +,-)$. (5.A.4)

The conduction electron propagator factors $(\sin\pi x)^{-1}$ are to be understood as the limit

$$\frac{1}{\sin\pi x} = \lim_{\epsilon \to 0^+} \frac{\theta(x-\epsilon)\,\theta(1-x-\epsilon)}{\sin\pi x} \quad ; \quad (5.A.5)$$

this ensures proper regularisation of the integrals in the infinite bandwidth limit.

To demonstrate that the limit $\epsilon \to 0$ exists, (5.A.3) is written as

$$(\beta\Delta)\int_\epsilon^{1/2} \frac{dx}{\sin\pi x}\cdot\left(\exp -\varepsilon^- x + \exp -\varepsilon^+ x\right)\left((1-x)^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right)$$
$$+ \left(\exp -\varepsilon^-(1-x) + \exp -\varepsilon^+(1-x)\right)\left(x^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right) . \quad (5.A.6)$$

Examine the limiting form of the integrand as $x \to 0$, where the integral is potentially singular:

$$\sim \frac{1}{\pi x}\left(2\left(1 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right) + \left(e^{-\varepsilon^+}+e^{-\varepsilon^-}\right)\left(\frac{-2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right) + O(x)\right)$$

$$\sim \frac{2}{\pi x}\left(\frac{2+e^{-\varepsilon^-}+e^{-\varepsilon^+} - 2 - \left(e^{-\varepsilon^-}+e^{-\varepsilon^+}\right)}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}} + O(x)\right)$$

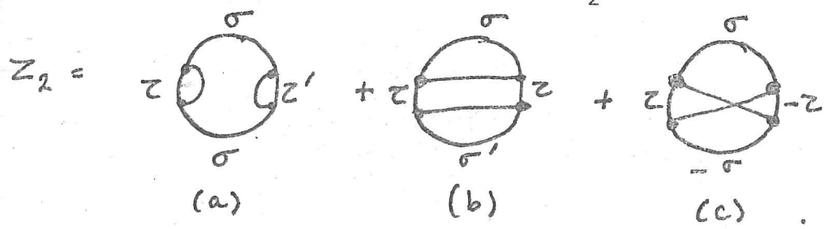
$$\sim O(1) \quad \text{as} \quad x \to 0 . \quad (5.A.7)$$

(5.A.3) is thus well-behaved as $\epsilon \to 0$.

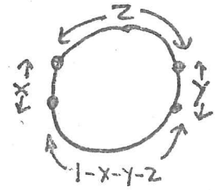
The second order term in (5.A.1) may be broken into two parts, one coming from second order terms of the partition function, the other from first order terms. The first part is

$$\frac{Z_2''}{Z_0''} - \frac{Z_2}{Z_0} \quad ; \quad (5.A.8)$$

this may in turn be broken into three parts, one from each of the three distinct diagrams (a), (b) and (c) making up Z_2:

$Z_2 =$  . (5.A.9)

The integration variables used in expressing these contributions will be x,y,z where they correspond to

 (5.A.10)

The integration volume is constrained by (i) $x \geq 0$, (ii) $y \geq 0$, (iii) $z \geq 0$, (iv) $1-x-y-z \geq 0$. To avoid double counting of identical diagrams, the further constraint $z \leq 1-x-y-z$ is imposed; this replaces (iv) by $1-x-y-2z \geq 0$.

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$$+ \left(\exp -\varepsilon^-(1-x) + \exp -\varepsilon^+(1-x)\right)\left(x^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right) \quad . \quad (5.A.6)$$

Examine the limiting form of the integrand as $x \to 0$, where the integral is potentially singular:

$$\sim \frac{1}{\pi x}\left(2\left(1 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right) + \left(e^{-\varepsilon^+}+e^{-\varepsilon^-}\right)\left(\frac{-2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right) + O(x)\right)$$

$$\sim \frac{2}{\pi x}\left(\frac{2+e^{-\varepsilon^-}+e^{-\varepsilon^+} - 2 - \left(e^{-\varepsilon^-}+e^{-\varepsilon^+}\right)}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}} + O(x)\right)$$

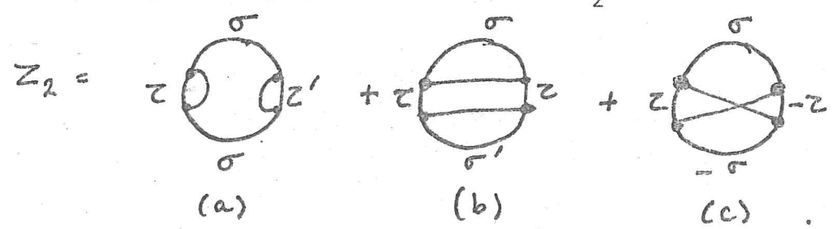
$$\sim O(1) \quad \text{as} \quad x \to 0 \, . \quad (5.A.7)$$

(5.A.3) is thus well-behaved as $\epsilon \to 0$.

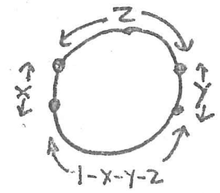
The second order term in (5.A.1) may be broken into two parts, one coming from second order terms of the partition function, the other from first order terms. The first part is

$$\frac{Z_2''}{Z_0''} - \frac{Z_2}{Z_0} \quad ; \quad (5.A.8)$$

this may in turn be broken into three parts, one from each of the three distinct diagrams (a), (b) and (c) making up Z_2:

$Z_2 =$  . (5.A.9)

The integration variables used in expressing these contributions will be x,y,z where they correspond to

 (5.A.10)

The integration volume is constrained by (i) $x \geq 0$, (ii) $y \geq 0$, (iii) $z \geq 0$, (iv) $1-x-y-z \geq 0$. To avoid double counting of identical diagrams, the further constraint $z \leq 1-x-y-z$ is imposed; this replaces (iv) by $1-x-y-2z \geq 0$.

These contributions to the second order term are, explicitly,

$$\frac{Z_2''}{Z_0''} - \frac{Z_2}{Z_0} = (\beta\Delta)^2 \int_0^1 dx \int_0^1 dy \int_0^{1/2} dz\ \Theta(1-x-y-2z)\ \cdot$$

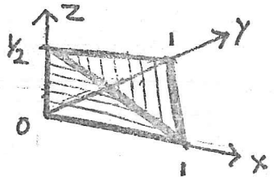
$$\left(\frac{\exp-\varepsilon^- x + \exp-\varepsilon^+ x}{\sin \pi x}\right)\left(\frac{\exp-\varepsilon^+ y + \exp-\varepsilon^- y}{\sin \pi y}\right)\left((1-x-y)^2 - \frac{2}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}\right) \quad (a)$$

$$+ \left(\frac{\exp-\varepsilon^-(x+y) + \exp-\varepsilon^+(x+y)}{\sin \pi z \cdot \sin \pi (x+y+z)}\right)\left((1-x-y)^2 + (1-x-y-2z)^2 - \frac{4}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}\right) \quad (b)$$

$$+ \left(\frac{\exp-\varepsilon^- x \exp-\varepsilon^+ y + \exp-\varepsilon^+ x \exp-\varepsilon^- y}{\sin \pi (z+x) \cdot \sin \pi (z+y)}\right)\left((1-x-y-2z)^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right) \quad (c)$$

(5.A.11)

The integration volume is the tetrahedron with vertices (000),(100),(010),(00½):



The integrand (a) diverges along faces x=0 and y=0; (b) diverges along the face z=0; (c) diverges along the edges x=z=0 and y=z=0.

The remaining term, which will be denoted (d), comes from first-order terms in the partition function expansion:

$$-\frac{Z_1}{Z_0}\left(\frac{Z_1''}{Z_0''} - \frac{Z_1}{Z_0}\right) = -(\beta\Delta)^2 \int_0^1 dx \left(\frac{\exp-\varepsilon^+ x + \exp-\varepsilon^- x}{\sin \pi x}\right)\left(\frac{2}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}\right) \cdot$$

$$\times \int_0^1 dy \left(\frac{\exp-\varepsilon^+ y + \exp-\varepsilon^- y}{\sin \pi y}\right)\left((1-y)^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right) \cdot \quad (d)$$

(5.A.12)

The x-integral is singular as $\epsilon \to 0$; the y integral is just (5.A.3) which was previously shown to be well behaved.

The individual terms (a), (b) and (d) are logarithmically divergent as $\epsilon \to 0$, though term (c) on its own exists in that limit. It will now be demonstrated that the total divergence of the sum of these terms cancels.

Term (a).

(i) do z-integral directly: (integrand is independent of z) :

$$\to \frac{1}{2}\int_\epsilon^{1-\epsilon} dx\ \frac{\exp-\varepsilon^- x + \exp-\varepsilon^+ x}{\sin \pi x} \int_\epsilon^{1-\epsilon} dy\ \frac{\exp-\varepsilon^- y + \exp-\varepsilon^+ y}{\sin \pi y}\ \Theta(1-x-y)\cdot(1-x-y)\cdot$$

$$\cdot\left((1-x-y)^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right) . \quad (5.A.13)$$

(ii) fold integration range into ($\frac{1}{2} \geq x \geq y \geq \epsilon$):

$$\to \int_\epsilon^{1/2} dx\ \frac{\exp-\varepsilon^+ x + \exp-\varepsilon^- x}{\sin \pi x} \int_\epsilon^x dy\ \frac{\exp-\varepsilon^+ y + \exp-\varepsilon^- y}{\sin \pi y}\left[(1-x-y)^3 - \frac{2}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}(1-x-y)\right]$$

$$+ \int_\epsilon^{1/2} dx\ \frac{\exp-\varepsilon^+(1-x) + \exp-\varepsilon^-(1-x)}{\sin \pi x} \int_\epsilon^x dy\ \frac{\exp-\varepsilon^+ y + \exp-\varepsilon^- y}{\sin \pi y}\left[(x-y)^3 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}(x-y)\right] \quad (5.A.14)$$

(iii) expand the y-integrals as

$$\int_\epsilon^{1/2} dx \int_\epsilon^x dy\ \frac{a(x)}{y} + b(x) + c(x)\,y \cdots \quad (5.A.15)$$

On integration, only the leading term a(x) contributes to the singularity of the integral; it gives rise to a factor $a(x)\ln(x/\epsilon)$. Only that part of a(x) that behaves like x^{-1} combines with the ln(x) factor to give a singular term. Collecting singular terms, (a) behaves as

$$-\frac{2}{\pi}\ln\epsilon \int_\epsilon^{1-\epsilon} dx\ \frac{\exp-\varepsilon^+ x + \exp-\varepsilon^- x}{\sin \pi x}\ (1-x)\left((1-x)^2 - \frac{2}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}\right)$$

$$-\frac{2}{\pi^2}\left(\frac{e^{-\varepsilon^+}+e^{-\varepsilon^-}}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}\right)\ln^2\epsilon + \text{constant} . \quad (5.A.16)$$

as $\epsilon \to 0$.

Term (b).

(i) Use the identities

$$\int_0^\infty dx \int_0^\infty dy\ f(x+y) \equiv \int_0^\infty x\, f(x)\, dx \qquad (5.A.17)$$

$$\frac{\sin \pi x}{\sin \pi z \sin \pi (z+x)} \equiv \cot \pi z - \cot \pi (z+x) . \qquad (5.A.18)$$

to write (b) as

$$\int_0^{1-2\epsilon} dx\ \frac{\exp -\varepsilon^- x + \exp -\varepsilon^+ x}{\sin \pi x} \cdot X \cdot \int_0^{1/2} dz\ \theta(1-x-2z)\,\theta(z-\epsilon)\,\theta(1-2-\epsilon)\,\theta(z+x-\epsilon) \cdot$$

$$\cdot\, \theta(1-z-x-\epsilon)\,\left(\cot \pi z - \cot \pi (z+x)\right)\left((1-x)^2+(1-x-2z)^2 - \frac{4}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}\right). \qquad (5.A.19)$$

Eliminating the superfluous θ-functions $\theta(1-z-\epsilon)$, $\theta(z+x-\epsilon)$, $\theta(1-z-x-\epsilon)$, and folding the range of the x-integral into $0 \le x \le \frac{1}{2}$:

$$\to \int_0^{1/2} dx\ \frac{\exp -\varepsilon^- x + \exp -\varepsilon^+ x}{\sin \pi x} \cdot X \cdot \int_\epsilon^{1/2 - x/2} dz\ \left(\cot \pi z - \cot \pi (z+x)\right)\left((1-x)^2+(1-x-2z)^2 - \frac{4}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}\right)$$

$$+ \int_{2\epsilon}^{1/2} dx\ \frac{\exp -\varepsilon^-(1-x) + \exp -\varepsilon^+(1-x)}{\sin \pi x} \cdot (1-x) \cdot \int_\epsilon^{x/2} dz\ \left(\cot \pi z + \cot \pi (z-x)\right)\left(x^2+(x-2z)^2 - \frac{4}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}\right). \qquad (5.A.20)$$

Using the same procedure as before (part (a)) to extract the singular part:

$$(b) \to\ -\frac{2}{\pi} \ln \epsilon \int_\epsilon^{1-\epsilon} dx\ \frac{\exp -\varepsilon^- x + \exp -\varepsilon^+ x}{\sin \pi x} \cdot X \cdot \left((1-x)^2 - \frac{2}{2+e^{-\varepsilon^+}+e^{-\varepsilon^-}}\right)$$

$$+ \left(\frac{e^{-\varepsilon^+}+e^{-\varepsilon^-}}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right)\frac{2}{\pi^2}\left((\ln \epsilon + \ln 2)^2 - 2\ln 2\right) + \text{constant}. \qquad (5.A.21)$$

Term (c).

The integrand of (c) is only divergent along edges of the integration volume, where the integral behaves as:

$$\int_0 dy\, a(y) \int_0 dx \int_0 dz\ \frac{\theta(x+z-\epsilon)}{x+z} \sim \int_0 dy\, a(y) \int_\epsilon dz' \cdot z' \sim \text{constant as } \epsilon \to 0. \qquad (5.A.22)$$

Term (c) is thus non-singular.

Adding (5.A.16) and (5.A.21) the total singular behaviour of terms (a), (b), and (c) as $\epsilon \to 0$ is

$$\lim_{\epsilon \to 0} (a)+(b)+(c) = -\frac{2}{\pi} \ln \epsilon \left[\int_\epsilon^{1-\epsilon} dx\ \frac{\exp -\varepsilon^+ x + \exp -\varepsilon^- x}{\sin \pi x} \cdot \left((1-x)^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right)\right]$$

$$+ \text{constant}. \qquad (5.A.23)$$

The integral is of course (5.A.3) which has been shown to be well-behaved.

Term (d).

(i) as before, fold the singular x-integral of (5.A.12) into the range $0 \le x \le \frac{1}{2}$:

$$\to\ -\frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}} \cdot \left(\int_\epsilon^{1/2} dx\ \frac{\exp -\varepsilon^- x + \exp -\varepsilon^+ x}{\sin \pi x} + \frac{\exp -\varepsilon^-(1-x) + \exp -\varepsilon^+(1-x)}{\sin \pi x}\right) \cdot$$

$$\cdot \left[\int_\epsilon^{1-\epsilon} dy\ \frac{\exp -\varepsilon^+ y + \exp -\varepsilon^- y}{\sin \pi y}\left((1-y)^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right)\right] . \qquad (5.A.24)$$

$$\sim +\frac{2}{\pi} \ln \epsilon \left[\int_\epsilon^{1-\epsilon} dy\ \frac{\exp -\varepsilon^+ y + \exp -\varepsilon^- y}{\sin \pi y}\left((1-y)^2 - \frac{2}{2+e^{-\varepsilon^-}+e^{-\varepsilon^+}}\right)\right]$$

$$+ \text{Constant}. \qquad (5.A.25)$$

The singularity of (5.A.25) exactly cancels that of (5.A.23) and thus the second order term (a)+(b)+(c)+(d) has been explicitly shown to exist in the limit $\epsilon \to 0$.

(II). Asymptotic evaluation to $O(\varepsilon^+,\varepsilon^-)^2$ for $|\varepsilon^+|,|\varepsilon^-| \ll 1$ (high temperature/free orbital limit).

(i) The prefactor (5.A.2) is

$$\beta\frac{Z_0''}{Z_0} = \frac{\beta}{4}\cdot\frac{2}{4-(\varepsilon^++\varepsilon^-)\ldots}$$

$$= \frac{\beta}{8}\left(1+\frac{(\varepsilon^++\varepsilon^-)}{4}+O(\varepsilon^+,\varepsilon^-)^2.\right) \qquad (5.A.26)$$

(ii) The first order term (5.A.3) is

$$\frac{Z_0''}{Z_0''}-\frac{Z_1}{Z_0} = (\beta\Delta)\int_0^1\frac{dx}{\sin\pi x}\,(2-(\varepsilon^-+\varepsilon^+)x)\left((1-x)^2-\frac{1}{2}\left(1+\frac{(\varepsilon^++\varepsilon^-)}{4}\right)\right)$$

$$= -2\left(\frac{\beta\Delta}{\pi}\right)\left(1+\frac{(\varepsilon^++\varepsilon^-)}{4}\right)A + O(\varepsilon^+,\varepsilon^-)^2 \qquad (5.A.27)$$

where

$$A = 2\pi\int_0^{1/2}\frac{dx}{\sin\pi x}\,x(1-x) = 0.85255\ldots \qquad (5.A.28)$$

The integral A cannot be evaluated analytically, and has been calculated numerically. It is associated with the broadening of a pole of the d-electron Greens function(due to hybridisation) from a δ-function to a Lorentzian at high temperatures .

The high temperature expansion is quite well behaved, and does not generate any logarithms. The second order term will therefore not be given here. The expansion for the susceptibility is:

$$\chi = \frac{\beta}{8}\left(\left[1+\left(\frac{\varepsilon^++\varepsilon^-}{4}\right)+\ldots\right]-2\left(\frac{\beta\Delta}{\pi}\right)A\left[1+\left(\frac{\varepsilon^++\varepsilon^-}{4}\right)\ldots\right]+O\left(\frac{\beta\Delta}{\pi}\right)^2\right). \qquad (5.A.29a)$$

$$= \frac{1}{8T}+\frac{1}{32T^2}\left(U-\frac{8A\Delta}{\pi}+O(\Delta^2)\right)+O\left(\frac{1}{T^3}\right), \quad (|\varepsilon_d|,\,U \ll T). \qquad (5.A.29b)$$

(III) Asymptotic evaluation to $O(1/\varepsilon^{+3},\varepsilon^{-2})$ for $\varepsilon^+ \gg 1$, $|\varepsilon^-| \ll 1$ (intermediate temperature/asymmetric orbital limit). 137

Technique used: all terms $\exp-\varepsilon^+$ are set to zero.

(i). The prefactor (5.A.2) is

$$\beta\frac{Z_0''}{Z_0} = \frac{1}{4T}\cdot\frac{2}{3-\varepsilon^-+\varepsilon^{-2}/2\ldots}$$

$$= \frac{\beta}{6}\left(1+\frac{\varepsilon^-}{3}-\frac{\varepsilon^{-2}}{18}+O(\varepsilon^-)^3\right). \qquad (5.A.30)$$

(ii). The first order term (5.A.3) is found by folding the integral into $0 < x < \frac{1}{2}$, and eliminating terms of order $\exp-\frac{1}{2}\varepsilon^+$ or less:

$$\frac{Z_1''}{Z_0''}-\frac{Z_1}{Z_0} = (\beta\Delta)\int_\epsilon^{1/2}\frac{dx}{\sin\pi x}\cdot\left(\exp-\varepsilon^+x+1-\varepsilon^-x\right)\left((1-x)^2-\frac{2}{3-\varepsilon^-}\right)$$

$$+\left(1-\varepsilon^-(1-x)\right)\left(x^2-\frac{2}{3-\varepsilon^-}\right)$$

$$= (\beta\Delta)\int_\epsilon^{1/2}\frac{dx}{\sin\pi x}\,\exp-\varepsilon^+x\left((1-x)^2-\frac{2}{3}\left(1+\frac{\varepsilon^-}{3}\right)\right) \qquad (a)$$

$$+(\beta\Delta)\int_\epsilon^{1/2}\frac{dx}{\sin\pi x}\cdot\left(-2x(1-x)-\frac{1}{3}\right)+\varepsilon^-\left(\frac{2}{9}-x(1-x)\right). \qquad (b) \qquad (5.A.31)$$

The first part (a) of the integral (5.A.31) is controlled by the exponential factor, and is determined by the behaviour at small x. Expanding $1/\sin\pi x$,

$$\frac{1}{\sin\pi x} = \frac{1}{\pi x}\left(1+\frac{1}{6}(\pi x)^2\ldots\right) \qquad (5.A.32)$$

(5.A.31a) becomes

$$\left(\frac{\beta\Delta}{\pi}\right)\int_\epsilon^\infty dx\,\frac{\exp-\varepsilon^+x}{x}\left(\frac{1}{3}-\frac{2}{9}\varepsilon^-\right)-2x+x^2\left)\left(1+\frac{1}{6}(\pi x)^2\ldots\right)\right.$$

$$=\left(\frac{\beta\Delta}{\pi}\right)\left(-\left(\frac{1}{3}-\frac{2}{9}\varepsilon^-\right)Ei(-\varepsilon^+\epsilon)-\frac{2}{\varepsilon^+}+\frac{1}{\varepsilon^{+2}}+O\left(\frac{1}{\varepsilon^{+3}}\right)\right). \qquad (5.A.33)$$

$E_i(x)$ is the Exponential-Integral function (Gradshteyn and Ryzhik, 1965; 8.21) given by

$$\int_x^\infty \frac{e^{-t}}{t} = -E_i(x) \qquad (5.A.34)$$

For small x:

$$E_i(x) = \mathbb{C} + \ln|x| + O(x); \quad \mathbb{C} = \text{Euler's constant} = 0.577215\ldots \qquad (5.A.35)$$

Part (b) of (5.A.31) is easily integrated, using the integral A defined in (5.A.28):

$$-\left(\frac{\beta\Delta}{\pi}\right)\cdot A\left(1+\frac{\epsilon^-}{2}\right) - \left(\frac{\beta\Delta}{\pi}\right)\left[\ln\tan\frac{\pi x}{2}\right]_\epsilon^{1/2}\cdot\left(\frac{1}{3}-\frac{2}{9}\epsilon^-\right) \qquad (5.A.36)$$

On expanding the exponential-integral function in (5.A.33) and adding (5.A.36), it can be seen that the $\ln\epsilon$ terms cancel and the sum is:

$$\frac{\beta\Delta}{\pi}\left\{-\left[\left(\frac{1}{3}-\frac{2}{9}\epsilon^-\ldots\right)\left(\mathbb{C}+\ln\left(\frac{2\epsilon^+}{\pi}\right)\right)\right] - A\left(1+\frac{\epsilon^-}{2}\ldots\right) - \frac{2}{\epsilon^+} + \frac{1}{\epsilon^{+2}} + O\left(\frac{1}{\epsilon^{+3}}\right)\right\} \qquad (5.A.37)$$

Note the $\ln\epsilon^+$ term that has appeared. The term A again represents broadening of the level ϵ^- near the Fermi level. The susceptibility is thus:

$$\chi = \frac{\beta}{6}\left(1+\frac{\epsilon^-}{3}-\frac{\epsilon^{-2}}{18} - \left(\frac{\beta\Delta}{\pi}\right)\left(\frac{1}{3}\left(1-\frac{\epsilon^-}{3}\right)\left(\ln\frac{2\epsilon^+}{\pi}+\mathbb{C}\right) + A\left(1+\frac{5}{6}\epsilon^-\right) + \frac{2}{\epsilon^+} - \frac{1}{\epsilon^{+2}}\right) + O\left(\frac{\beta\Delta}{\pi}\right)^2\right) + O\left(\frac{1}{\epsilon^{+3}}, \epsilon^{-2}\right) \qquad (5.A.38a)$$

Or in more physical terms:

$$\chi = \frac{1}{6T}\left[1-\frac{2\Delta}{\pi u}+O\left(\frac{\Delta}{u}\right)^2\right] - \frac{1}{18T^2}\left[E_d - \frac{\Delta}{\pi}\ln\left(\frac{T}{\alpha u}\right) + \frac{3A\Delta}{\pi}\right] + O\left(\frac{(E_d,\Delta)^2}{T^3}\right) + \left[\frac{\Delta}{6\pi u^2}+O\left(\frac{\Delta^2}{u^3}\right)\right] + O\left(\frac{\Delta T}{U^3}\right). \qquad (u\gg T,\ |E_d|<T). \qquad (5.A.38b)$$

where $\alpha = \frac{2}{\pi}\exp\mathbb{C}$. The second order term is complicated, and as the logarithmic nature of the series is shown up by the first order term, will not be given here.

(iv) Asymptotic evaluation to $O(1/\epsilon^+, 1/\epsilon^-)^4$ for $\epsilon^+, \epsilon^- \gg 1$ (low temperature/Kondo limit).

Technique: set all terms with factors like $\exp-\epsilon^+$, $\exp-\epsilon^-$ equal to zero.

(i) The prefactor (5.A.2) is

$$\frac{\beta Z_0''}{Z_0} = \frac{\beta}{4} \qquad (5.A.39)$$

(ii) the first order term (5.A.3) is (after folding into $(0,\frac{1}{2})$ and rejecting exponentially suppressed terms):

$$\frac{Z_1''}{Z_0''} - \frac{Z_1}{Z_0} = (\beta\Delta)\int_\epsilon^{1/2} \frac{dx}{\sin\pi x}\left(\exp-\epsilon^- x + \exp-\epsilon^+ x\right)\left((1-x)^2-1\right)$$

$$= \left(\frac{\beta\Delta}{\pi}\right)\int_\epsilon^\infty \frac{dx}{x}\left(\exp-\epsilon^- x + \exp-\epsilon^+ x\right)\left(-2x+x^2+O(x^3)\right)$$

$$= \left(\frac{\beta\Delta}{\pi}\right)\left[-2\left(\frac{1}{\epsilon^+}+\frac{1}{\epsilon^-}\right) + \left(\frac{1}{\epsilon^{+2}}+\frac{1}{\epsilon^{-2}}\right) + O\left(\frac{1}{\epsilon^+},\frac{1}{\epsilon^-}\right)^3\right] \qquad (5.A.40)$$

In this case the logarithmic Kondo-type terms only enter in second order terms: these must now be calculated.

(iii) Some necessary integrals; references (GR....) are to Gradshteyn and Ryzhik (1965).

(a) $$\int_0^\infty dx\, x^n \ln x \exp-\alpha x = \frac{n!}{\alpha^{n+1}}\left(\sum_{r=1}^n \frac{1}{r} - \mathbb{C} - \ln\alpha\right) \quad [GR\,4.352]$$

($\mathbb{C}$ = Eulers Constant, 0.577..)

(b) $$\int_x^\infty \frac{dx'}{x'}\exp-\alpha x' = -E_i(-\alpha x) \quad [GR\,8.211]$$

(c) $$E_i(x) = \mathbb{C} + \ln|x| + O(x) \quad [GR\,8.214]$$

(d) $$\int_0^{1/2} dx\left(\frac{\pi^2}{\sin^2\pi x} - \frac{1}{x^2}\right) = 2$$

(e) $$\int_0^{1/2} dx\left(\frac{\pi^2}{\sin^2\pi x} - \frac{1}{x^2}\right)x(1-x) = 3/2 - \ln\pi \quad (\text{uses } [GR\,3.747/7]) \qquad (5.A.41)$$

(iv) Evaluation of the second order term. As in section I this term is broken up into four parts - (a),(b) and (c) of (5.A.11) and (d) of (5.A.12).

Term (a) becomes (after doing the z-integral, folding into integration range $(0,\frac{1}{2})$, and removing exponentially small terms)

$$\frac{(\beta\Delta)^2}{2}\int_{\epsilon}^{1/2} dx\ \frac{\exp-\varepsilon^- x+\exp-\varepsilon^+ x}{\sin\pi x}\int_{\epsilon}^{1/2} dy\ \frac{\exp-\varepsilon^- y+\exp-\varepsilon^+ y}{\sin\pi y}\left[(1-x-y)^3-(1-x-y)\right] \tag{5.A.42}$$

Using the symmetry in $x\leftrightarrow y$, and expanding $1/\sin\pi x$, (a) becomes:

$$(\beta\Delta)^2\int_{6}^{\infty} dx\ \frac{\exp-\varepsilon^- x+\exp-\varepsilon^+ x}{\pi x}\cdot\left(1+\frac{(\pi x)^2}{6}\dots\right)\int_{\epsilon}^{\infty} dy\ \frac{\exp-\varepsilon^- y+\exp-\varepsilon^+ y}{\pi y}\left(1+\frac{(\pi y)^2}{6}\dots\right).$$

$$\cdot\ x\left(-x^2+3x-2-3xy+3y\right) \tag{5.A.43}$$

At this point, it is convenient to combine term (a) with term (d).

Term (d) is

$$-(\beta\Delta)^2\int_{6}^{\infty}\frac{dx}{\pi x}\left(\exp-\varepsilon^- x+\exp-\varepsilon^+ x\right)\left(1+\frac{(\pi x)^2}{6}\dots\right)\int_{\epsilon}^{\infty}\frac{dy}{\pi y}\left(\exp-\varepsilon^+ y+\exp-\varepsilon^- y\right)\left(1+\frac{(\pi y)^2}{6}\dots\right).$$

$$\cdot\ x(x-2). \tag{5.A.44}$$

Combining (5.A.43,44) and keeping terms up to $0(1/\varepsilon^4)$:

$$\left(\frac{\beta\Delta}{\pi}\right)^2\int_{0}^{\infty} dx\ (\exp-\varepsilon^- x+\exp-\varepsilon^+ x)(2x-x^2+o(x^3))\int_{\epsilon}^{\infty} dy\ \frac{\exp-\varepsilon^- y+\exp-\varepsilon^+ y}{y}$$

$$+\left(\frac{\beta\Delta}{\pi}\right)^2\int_{0}^{\infty} dx\ (\exp-\varepsilon^- x+\exp-\varepsilon^+ x)(3-3x+o(x^2))\int_{\epsilon}^{\infty} dy\ \exp-\varepsilon^- y+\exp-\varepsilon^+ y\,(1+o(y^2)) \tag{5.A.45}$$

Evaluating, using (5.A.41 b,c) , the contribution from terms (a) and (d) is:

$$\left(\frac{\beta\Delta}{\pi}\right)^2\left\{-2\left[\left(\frac{1}{\varepsilon^{-2}}+\frac{1}{\varepsilon^{+2}}\right)-\left(\frac{1}{\varepsilon^{-3}}+\frac{1}{\varepsilon^{+3}}\right)\right]\left[2C+\ln\varepsilon^-+\ln\varepsilon^++2\ln\epsilon\right]+3\left(\frac{1}{\varepsilon^-}+\frac{1}{\varepsilon^+}\right)^2-3\left(\frac{1}{\varepsilon^-}+\frac{1}{\varepsilon^+}\right)\left(\frac{1}{\varepsilon^{-2}}+\frac{1}{\varepsilon^{+2}}\right)\right\}$$

$$+\ o\left(\frac{1}{\varepsilon^-},\frac{1}{\varepsilon^+}\right)^4 \tag{5.A.46}$$

Term (b) . Using the identity (5.A.17), and suppressing exponentially small terms, (b) becomes:

$$(\beta\Delta)^2\int_{0}^{\infty} dx\ x\,(\exp-\varepsilon^- x+\exp-\varepsilon^+ x)\int_{\epsilon}^{1/2-(x/2)} dz\ \frac{\theta(1-x-2z)}{\sin\pi z\sin\pi(x+z)}\cdot\left[(1-x)^2+(1-x-2z)^2-2\right] \tag{5.A.47}$$

This may be simplified using the identity

$$\frac{\pi^2}{\sinh\pi z\sin\pi(z+x)} \equiv \frac{1}{z(z+x)}+\left(\frac{\pi^2}{\sin\pi z\sin\pi(z+x)}-\frac{1}{z(z+x)}\right)$$

$$=\frac{1}{xz}-\frac{1}{x(z+x)}+\left(\frac{\pi^2}{\sin^2\pi z}-\frac{1}{z^2}\right)+\frac{1}{2}x\frac{d}{dz}\left(\frac{\pi^2}{\sin^2\pi z}-\frac{1}{z^2}\right)+o(x^2). \tag{5.A.48}$$

(b) becomes:

$$\left(\frac{\beta\Delta}{\pi}\right)^2\int_{0}^{\infty} dx\cdot x\left(\exp-\varepsilon^- x+\exp-\varepsilon^+ x\right)\cdot$$

$$\left[2\int_{\epsilon}^{1/2} dz\left(\frac{1}{z}-\frac{1}{z+x}\right)\frac{(1-x)^2-1}{x}+\int_{0}^{1/2} dz\ \frac{(4z^2-4z(1-x))}{x}\left(\frac{1}{z}-\frac{1}{z+x}\right)\right.$$

$$+2\left((1-x)^2-1\right)\int_{0}^{1/2} dz\left(\frac{\pi^2}{\sin^2\pi z}-\frac{1}{z^2}\right)-4\int_{0}^{1/2} dz\ z(1-z)\left(\frac{\pi^2}{\sin^2\pi z}-\frac{1}{z^2}\right)$$

$$\left.+\ x\int_{0}^{1/2} dz\left(4z\left(\frac{\pi^2}{\sin^2\pi z}-\frac{1}{z^2}\right)+\left(2z^2-2z\right)\frac{d}{dz}\left(\frac{\pi^2}{\sin^2\pi z}-\frac{1}{z^2}\right)\right)+\frac{\pi^2}{2}x+o(x^2)\right] \tag{5.A.49}$$

evaluating the z-integrals with the help of (5.A.41) ,(b) becomes :

$$\left(\frac{\beta\Delta}{\pi}\right)^2\int_{0}^{\infty} dx\left(\exp-\varepsilon^- x+\exp-\varepsilon^+ x\right)\left(\begin{array}{l}2x^2\ln x-4x-2x^2+4x\ln 2\pi\\+(4x-2x^2)\ln\epsilon+o(x3)\end{array}\right) \tag{5.A.50}$$

Finally, (b) is

$$\left(\frac{\beta\Delta}{\pi}\right)^2\left\{\left[\left(\frac{1}{\varepsilon^{+2}}+\frac{1}{\varepsilon^{-2}}\right)-\left(\frac{1}{\varepsilon^{+3}}+\frac{1}{\varepsilon^{-3}}\right)\right](4\ln\epsilon)+\left(\frac{1}{\varepsilon^{+2}}+\frac{1}{\varepsilon^{-2}}\right)(4\ln 2\pi-4)-\left(\frac{1}{\varepsilon^{+3}}+\frac{1}{\varepsilon^{-3}}\right)(4C-2)\right.$$

$$\left.-4\left(\frac{\ln\varepsilon^-}{\varepsilon^{-3}}+\frac{\ln\varepsilon^+}{\varepsilon^{+3}}\right)+o\left(\frac{1}{\varepsilon^+},\frac{1}{\varepsilon^-}\right)^4\right\} \tag{5.A.51}$$

Term (c). Recall that this term is non-singular. Suppressing small terms, (c) becomes:

$$(\beta\Delta)^2 \int_0^\infty dx \int_0^\infty dy \left[(\exp-\varepsilon^+ x \exp-\varepsilon^- y) + (\exp-\varepsilon^- x \exp-\varepsilon^+ y)\right] \int_0^{1/2 - \frac{(x+y)}{2}} dz \; \frac{1}{\sinh\pi(z+y)\sin\pi(z+x)} \left[(1-x-y-2z)^2 - 1\right] \tag{5.A.52}$$

As with (b), the z-integral may be simplified using the identity:

$$\frac{\pi^2}{\sin\pi(z+x)\sin\pi(z+y)} \equiv \frac{1}{(z+x)(z+y)} + \left(\frac{\pi^2}{\sin^2\pi z} - \frac{1}{z^2}\right) + \frac{1}{2}(x+y)\frac{d}{dz}\left(\frac{\pi^2}{\sin^2\pi z} - \frac{1}{z^2}\right) + O(x,y)^2 \tag{5.A.53}$$

(c) becomes:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \int_0^\infty dx \int_0^\infty dy \left(\exp-\varepsilon^+ x \exp-\varepsilon^- y + \exp-\varepsilon^- x \exp-\varepsilon^+ y\right) \cdot$$

$$\left[\int_0^{1/2} dz \; \frac{(z+x)^2 + (z+y)^2 + 2(z+x)(z+y) - 2(z+x) - 2(z+y)}{(z+x)(z+y)} - \int_0^{1/2} dz \left(\frac{\pi^2}{\sin^2\pi z} - \frac{1}{z^2}\right) 4z(1-z)\right.$$

$$\left. + 2(x+y)\int_0^{1/2} dz \left[(z^2 - z)\frac{d}{dz}\left(\frac{\pi^2}{\sin^2\pi z} - \frac{1}{z^2}\right) + (2z-1)\left(\frac{\pi^2}{\sin^2\pi z} - \frac{1}{z^2}\right)\right] + \frac{\pi^2}{2}(x+y) + O(x,y)^2\right] \tag{5.A.54}$$

Evaluating the z-integrals with the help of (5.A.41), (c) becomes:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \int_0^\infty dx \int_0^\infty dy \left(\exp-\varepsilon^+ x \exp-\varepsilon^- y + \exp-\varepsilon^- x \exp-\varepsilon^+ y\right) \cdot \begin{pmatrix} -4 + 4\ln 2\pi - 2(x+y) \\ +(2+x-y)\ln x + (2+y-x)\ln y \\ + O(x,y)^2 \end{pmatrix} \tag{5.A.55}$$

Finally, one obtains:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \left[\frac{-4}{\varepsilon^+\varepsilon^-}\left(\ln\frac{\varepsilon^+}{2\pi} + \ln\frac{\varepsilon^-}{2\pi} + 2C - 2\right) - \frac{2}{\varepsilon^+\varepsilon^-}\left(\frac{1}{\varepsilon^+} + \frac{1}{\varepsilon^-}\right)\right.$$

$$\left. + \frac{2}{\varepsilon^+\varepsilon^-}\left(\frac{\ln\varepsilon^+}{\varepsilon^-} - \frac{\ln\varepsilon^+}{\varepsilon^+} + \frac{\ln\varepsilon^-}{\varepsilon^+} - \frac{\ln\varepsilon^-}{\varepsilon^-}\right) + O\left(\frac{1}{\varepsilon^+}, \frac{1}{\varepsilon^-}\right)^4\right] \tag{5.A.56}$$

This completes the evaluation of the second order term.

Finally, one can sum the four contributions (a), (b), (c) and (d). This is the sum of (5.A.46), (5.A.51), and (5.A.56). The singular terms of order $\ln\epsilon$ that blow up as the bandwidth goes to infinity all cancel, as they must, and one is left with:

$$-\left(\frac{\beta\Delta}{\pi}\right)^2 \frac{1}{4}\left(\frac{1}{\varepsilon^+} + \frac{1}{\varepsilon^-}\right)^2 \left(\frac{1}{2}\ln\frac{\varepsilon^+}{2\pi} + \frac{1}{2}\ln\frac{\varepsilon^-}{2\pi} + C + \frac{1}{4}\right)$$

$$-\left(\frac{\beta\Delta}{\pi}\right)^2 \left[\frac{1}{\varepsilon^{+3}} + \frac{1}{\varepsilon^{-3}} + \frac{5}{\varepsilon^+\varepsilon^-}\left(\frac{1}{\varepsilon^+} + \frac{1}{\varepsilon^-}\right) + 2\left(\frac{1}{\varepsilon^+} + \frac{1}{\varepsilon^-}\right)\left(\frac{1}{\varepsilon^{+2}} - \frac{1}{\varepsilon^{-2}}\right)\ln\left(\frac{\varepsilon^+}{\varepsilon^-}\right)\right]$$

$$+ O\left(\frac{1}{\varepsilon^+}, \frac{1}{\varepsilon^-}\right)^4 . \tag{5.A.57}$$

Constructing the whole series by adding the first order term (5.A.40), one sees that that two distinct contributions to the susceptiblity, "χ^{Kondo}" and "χ^{Pauli}", coming respectively from the leading and next-leading terms, may be distinguished:

$$\chi^{\text{Kondo}}(T) = \frac{1}{4T}\left(1 + (J\rho)^{\text{eff}} + (J\rho)^{\text{eff}\,2}\ln\left(\frac{T}{D_{\text{eff}}}\right) \cdots\right) \tag{5.A.58}$$

where

$$(J\rho)^{\text{eff}} = \frac{2\Delta}{\pi}\left(\frac{1}{E_d} - \frac{1}{E_d+u}\right); \quad D^{\text{eff}} = \frac{1}{2\pi}\exp\left(C + \frac{1}{4}\right)\left(-E_d(E_d+u)\right)^{1/2} \tag{5.A.59}$$

This corresponds to a Kondo temperature (Wilson's (1975) definition) of

$$T_K = \frac{1}{2\pi}\exp\left(C + \frac{1}{4}\right)(\Delta u)^{1/2}\exp\left[\frac{E_d(E_d+u)}{(2\Delta u/\pi)}\right] . \tag{5.A.60}$$

$\chi^{\text{Kondo}}(T)$ may be identified with spin fluctuations, and is expected from the Schrieffer-Wolff transformation; χ^{Pauli} may likewise be identified with the residual charge fluctuation processes, and is temperature independent. The correction terms $O(1/\varepsilon^+, 1/\varepsilon^-)^4$ give rise to a contribution linear in temperature.

$$\chi^{\text{Pauli}} = \frac{\Delta}{4\pi}\left(\frac{1}{E_d^2} + \frac{1}{(E_d+u)^2}\right) + \frac{1}{4}\left(\frac{\Delta}{\pi}\right)^2 \left\{\frac{1}{E_d^3} - \frac{1}{(E_d+u)^3} - \frac{5}{E_d(E_d+u)}\left(\frac{1}{E_d} - \frac{1}{E_d+u}\right)\right.$$

$$\left. + 2\left(\frac{1}{E_d} - \frac{1}{E_d+u}\right)\left(\frac{1}{(E_d+u)^2} - \frac{1}{E_d^2}\right)\ln\left|\frac{E_d+u}{E_d}\right|\right\} \cdots \tag{5.A.61}$$

$$\chi(T) = \chi^{\text{Kondo}}(T) + \chi^{\text{Pauli}} + O(T). \qquad (-E_d, E_d+u \gg T) \tag{5.A.62}$$

(v) Asymptotic evaluation to $O(1/\varepsilon^+, 1/\varepsilon^-)^4$ for $\varepsilon_3^+ - \varepsilon^- \gg 1$ (low temperature/non-magnetic orbital limit).

(i) The prefactor (5.A.2) becomes:

$$\beta \frac{Z_0''}{Z_0} = \frac{\beta}{2} \exp \varepsilon^- = \frac{\beta}{2} \exp -|\varepsilon^-| \tag{5.A.63}$$

The prescription for the higher order terms is thus to keep only terms with the exponentially large factor $\exp +|\varepsilon^-|$.

(ii) The first order term (5.A.3) becomes

$$(\beta\Delta) \int_{1/2}^{1} \frac{dx}{\sin \pi x} \exp -\varepsilon^- \exp -|\varepsilon^-|(1-x) \cdot (1-x)^2$$

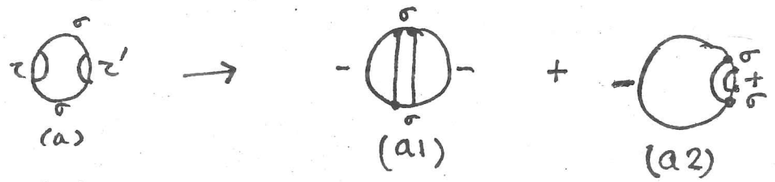
$$\rightarrow \left(\frac{\beta\Delta}{\pi}\right) \exp +|\varepsilon^-| \int_0^\infty \frac{dx}{x} \cdot \left(1 + \frac{(\pi x)^2}{6} \ldots\right) \exp -|\varepsilon^-| x \cdot x^2$$

$$= \left(\frac{\beta\Delta}{\pi}\right) \cdot \frac{\exp +|\varepsilon^-|}{\varepsilon^{-2}} + O\left(\frac{1}{\varepsilon^-}\right)^3 . \tag{5.A.64}$$

Again, logarithmic terms only enter into this temperature independent, Pauli-type susceptibilty series in second order, which is now calculated.

(iii) The second order terms (5.A.11) and (5.A.12) are again broken into the four parts (a)-(d).

Term (a). In this case (a) must be subdivided into two parts (a1) and (a2), shown diagrammatically:



(5.A.65)

Term (a1); doing the z-integral, one gets

$$(\beta\Delta)^2 \int_\epsilon^{1-\epsilon} dx \int_\epsilon^{1-\epsilon} dy\, \Theta(1-x-y)\, \frac{\exp -\varepsilon^-(x+y)}{\sin \pi x \sin \pi y} \cdot \frac{(1-x-y)^3}{2} \tag{5.A.66}$$

Transform $x \rightarrow 1-y-z$, and fold the y-integral into $(0, \frac{1}{2})$:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp +|\varepsilon^-| \int_0^\infty dz \exp -|\varepsilon^-| z \cdot \frac{z^3}{2} \int_0^{1/2} dy \left(\frac{\pi^2 \Theta(y-\epsilon)}{\sin \pi y \sin \pi (y+z)} + \frac{\pi^2 \Theta(y-z-\epsilon)}{\sin \pi y \sin \pi (y-z)} \right)$$

Expanding the 1/sin terms: (5.A.67)

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp +|\varepsilon^-| \int_0^\infty dz \exp -|\varepsilon^-| z \cdot \frac{z^3}{2} \left(\int_\epsilon^\infty \frac{2}{y(y+z)} + O(1) \right) \tag{5.A.68}$$

The y-integral may now be done:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp +|\varepsilon^-| \int_0^\infty dz \exp -|\varepsilon^-| z \cdot \frac{z^3}{2} \cdot \left(\frac{2}{z} \ln z/\epsilon + O(1) \right) \tag{5.A.69}$$

Finally completing the z-integration, the term (a1) yields:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp +|\varepsilon^-| \left(-\frac{3}{\varepsilon^{-3}} + \frac{2}{\varepsilon^{-3}} \left(\ln|\varepsilon^-| + C + \ln\epsilon \right) + O\left(\frac{1}{\varepsilon^-}\right)^4 \right) \tag{5.A.70}$$

Term (a2):

$$2(\beta\Delta)^2 \int_\epsilon^{1-\epsilon} dx \int_\epsilon^{1-\epsilon} dy\, \Theta(1-x-y) \cdot \frac{\exp -\varepsilon^- x \exp -\varepsilon^+ y}{\sin \pi x \sin \pi y} \frac{(1-x-y)^3}{2} ; \tag{5.A.71}$$

transforming $x \rightarrow 1-x$, and expanding 1/sin, etc:

$$\rightarrow \left(\frac{\beta\Delta}{\pi}\right)^2 \exp +|\varepsilon^-| \int_\epsilon^\infty dx \int_\epsilon^\infty dy \exp -|\varepsilon^-| x \exp -\varepsilon^+ y \cdot \frac{(x-y)^3}{xy} \left(1 + O(x,y)^2\right) \Theta(x-y) \tag{5.A.72}$$

Separating the integral into manageable parts yields:

$$\int_0^\infty dx \exp -|\varepsilon^-| x \int_0^x dy \exp -\varepsilon^+ y \,(-3x+3y)$$

$$\int_0^\infty dy \frac{\exp -\varepsilon^+ y}{y} \int_y^\infty dy \exp -|\varepsilon^-| x \cdot x^2$$

$$\int_\epsilon^\infty dx \frac{\exp -|\varepsilon^-| x}{x} \int_0^x dy \exp -\varepsilon^+ y \cdot y^2 . \tag{5.A.73}$$

Integrating over the first variable:

$$\int_{\epsilon}^{\infty} dx\ \exp-|\varepsilon^-|x\left(\frac{3}{\varepsilon^{+2}} - \frac{3x}{\varepsilon^+} - \frac{2}{\varepsilon^{+3}x}\right)$$

$$+ \int_{\epsilon}^{\infty} dx\ \exp-(|\varepsilon^-|+\varepsilon^+)x \cdot \left(\cdot\left(\frac{1}{\varepsilon^+}+\frac{1}{|\varepsilon^-|}\right)x + \left(\frac{2}{|\varepsilon^-|^2} - \frac{1}{\varepsilon^{+2}}\right) + \left(\frac{2}{\varepsilon^{+3}}+\frac{2}{|\varepsilon^-|^3}\right)\frac{1}{x}\right) \qquad (5.A.74)$$

Finally completing the integration of term (a2):

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp+|\varepsilon^-|\left\{\frac{2}{\varepsilon^{+3}}\ln\left|\frac{\varepsilon^-}{\varepsilon^+\varepsilon^-}\right| + \frac{2}{\varepsilon^{-3}}\left(\ln\epsilon + \ln|\varepsilon^+\varepsilon^-| + C\right)\right.$$

$$\left. - \frac{1}{\varepsilon^+\varepsilon^{-2}} - \frac{2}{\varepsilon^{+2}\varepsilon^-} + O\left(\frac{1}{\varepsilon}\right)^4\right\}. \qquad (5.A.75)$$

Term (b)

$$(\beta\Delta)^2 \int_0^1 dx \int_0^1 dy \int_{\epsilon}^{1/2} dz\ \frac{\theta(1-x-y-2z)}{\sin\pi z \sin\pi(x+y+z)}\ \exp-\varepsilon z(x+y)\ \left((1-x-y)^2+(1-x-y-2z)^2\right) \qquad (5.A.76)$$

Put $x' = x+y$, then $x'' = 1-x'$:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp+|\varepsilon^-| \int_{\epsilon}^{\infty} dx\ (1-x)\exp-|\varepsilon^-|x \int_{\epsilon}^{x/2} dz\ \frac{\pi^2}{\sin\pi z \sin\pi(x-z)} \cdot \left((x-2z)^2+x^2\right) \qquad (5.A.77)$$

Expanding the functions 1/sin:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp+|\varepsilon^-| \int_{2\epsilon}^{\infty} dx\ (1-x)\exp-|\varepsilon^-|x \int_{\epsilon}^{x/2} dz \left(\frac{x^2+z^2+(x-z)^2-2z(x-z)}{z(x-z)}\right)\left(1+o(x,z)^2\right) \qquad (5.A.78)$$

Doing the z-integral:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp+|\varepsilon^-| \int_0^{\infty} dx\ (1-x)\exp-|\varepsilon^-|x \cdot\ 2x\left(\ln x - \ln\epsilon - 1\right) \qquad (5.A.79)$$

Finally, the contribution of term (b) is:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp+|\varepsilon^-|\left\{-\left(\frac{2}{\varepsilon^{-2}}+\frac{4}{\varepsilon^{-3}}\right)\left(\ln\epsilon + \ln|\varepsilon^-| + C\right) + \frac{2}{\varepsilon^{-3}} + O\left(\frac{1}{\varepsilon}\right)^4\right\} \qquad (5.A.80)$$

Term (c).

$$2(\beta\Delta)^2 \int_0^1 dx \int_0^1 dy \int_0^{1/2} dz\ \theta(1-x-y-z)\ \exp-\varepsilon^- x\ \exp-\varepsilon^+ y\ (1-x-y-2z)^2 . \qquad (5.A.81)$$

Put $x' = 1-x$, and expand 1/sin :

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp+|\varepsilon^-| \int_0^{\infty} dx\ \exp-|\varepsilon^-|x \int_0^{\infty} dy\ \exp-\varepsilon^+ y\ \theta(x-y) \int_0^{\frac{x-y}{2}} dz\ \frac{(x-y-2z)^2}{(x-z)(y+z)}\left(1+o(x,y,z)^2\right) \qquad (5.A.82)$$

In doing the z-integral, one obtains

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp+|\varepsilon^-| \int_0^{\infty} dx\ \exp-|\varepsilon^-|x \int_0^{x} dy\ \exp-\varepsilon^+ y\ \left((x+y)(\ln x - \ln y) - 2(x-y) + o(x,y)^2\right) \qquad (5.A.83)$$

The remaining integral is conveniently split into two terms:

$$\int_0^{\infty} dx\ \exp-|\varepsilon^-|x \int_0^{x} dy\ \exp-\varepsilon^+ y \cdot\ (x+y)\ln x - 2(x-y)$$

$$- \int_0^{\infty} dy\ \exp-\varepsilon^+ y \int_x^{\infty} dx\ \exp-|\varepsilon^-|x \cdot (x+y)\ln y \qquad (5.A.84)$$

In doing the first integral, one obtains:

$$\int_0^{\infty} dx\ \exp-|\varepsilon^-|x \cdot \left(\frac{x}{\varepsilon^+}\ln x - \frac{2}{\varepsilon^+} + \frac{\ln x}{\varepsilon^{+2}} + \frac{2}{\varepsilon^{+2}}\right)$$

$$\int_0^{\infty} dx\ \exp-(\varepsilon^+ + |\varepsilon^-|)x \left(-2\left(\frac{1}{\varepsilon^+}+\frac{1}{|\varepsilon^-|}\right)x\ln x - \left(\frac{1}{\varepsilon^{+2}}+\frac{1}{|\varepsilon^-|^2}\right)\ln x - \frac{2}{\varepsilon^{+2}}\right) \qquad (5.A.85)$$

These two integrals may be evaluated to give the contribution from term (c):

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp+|\varepsilon^-|\left\{\left(\frac{2}{\varepsilon^{+2}\varepsilon^-} - \frac{2}{\varepsilon^+\varepsilon^{-2}}\right)\ln\left|\frac{\varepsilon^-}{\varepsilon^+-\varepsilon^-}\right| - \frac{2}{\varepsilon^+\varepsilon^{-2}} + O\left(\frac{1}{\varepsilon}\right)^4\right\} \qquad (5.A.86)$$

Finally, the contribution from <u>term (d)</u> is calculated:

$$-(\beta\Delta)^2 \int_{\epsilon}^{1-\epsilon} dx \; \frac{\exp -\varepsilon^- x}{\sin \pi x} \cdot 2 \exp -|\varepsilon^-| \int_0^1 \frac{dy}{\sin \pi y} \exp -\varepsilon^- y \cdot (1-y)^2 \qquad (5.A.86)$$

putting $x' = 1-x$, $y' = 1-y$, and expanding 1/sin :

$$-\left(\frac{\beta\Delta}{\pi}\right)^2 \exp -|\varepsilon^-| \cdot \int_{\epsilon}^{\infty} dx \; \frac{2}{x} \exp -|\varepsilon^-| x \cdot (1+O(x^2)) \int_0^{\infty} \frac{dy}{y} \exp -|\varepsilon^-| y \cdot y^2 (1+O(y^2)) \qquad (5.A.87)$$

Evaluating the integrals, the contribution from term (d) is:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp -|\varepsilon^-| \left[\frac{2}{\varepsilon^{-2}} \left(\ln |\varepsilon^-| + \ln \epsilon + C \right) \right] \qquad (5.A.88)$$

The contributions from terms (a1), (a2), (b), (c), and (d), namely (5.A.70), (5.A.75), (5.A.80), (5.A.86) and (5.A.88), must now be added to give the complete second order term. The singular $\ln\epsilon$ terms cancel, as do all terms of order $(1/\epsilon^2)$, leaving:

$$\left(\frac{\beta\Delta}{\pi}\right)^2 \exp -|\varepsilon^-| \left\{ \frac{-1}{\varepsilon^{-3}} \; \frac{-3}{\varepsilon^+ \varepsilon^{-2}} \; \frac{-2}{\varepsilon^{+2} \varepsilon^-} + 2 \left(\frac{1}{\varepsilon^+} + \frac{1}{\varepsilon^-} \right) \left(\frac{1}{\varepsilon^{+2}} - \frac{1}{\varepsilon^{-2}} \right) \ln \left| \frac{\varepsilon^-}{\varepsilon^+ - \varepsilon^-} \right| + O\left(\frac{1}{\varepsilon^3}\right) \right\}$$

(5.A.89)

A test of this evaluation is that the second order term (5.A.89) vanishes when $U = 0$, i.e., $\varepsilon^+ = -\varepsilon^-$. Writing out the full series, these leading terms are found to represent a temperature independent Pauli susceptibility.

$$\chi^{\text{Pauli}} = \frac{\Delta}{2\pi E_d^2} + \frac{1}{2}\left(\frac{\Delta}{\pi}\right)^2 \left\{ \frac{1}{E_d^3} \; \frac{-3}{E_d^2 (E_d+U)} + \frac{2}{E_d (E_d+U)^2} - 2\left(\frac{1}{E_d+U} - \frac{1}{E_d} \right) \left(\frac{1}{(E_d+U)^2} - \frac{1}{E_d^2} \right) \ln \left(\frac{2E_d+U}{E_d} \right) \right\}$$

$$+ O(\Delta^3) \cdots \qquad (+ O(T)) \qquad (5.A.90)$$

$(E_d, E_d+U \gg T)$.

CHAPTER SIX

SCALING THEORIES OF THE ANDERSON MODEL

6.1 The Scaling Approach.

The idea of scaling, or the renormalisation group (RG) has long been used as a formal device in field theory for dealing with infra-red divergences in perturbation theory (Bogoliubov and Shirkov (1959)), If a perturbation expansion for the low energy properties of a model (such as the static susceptibility of the Kondo model) has logarithmic infra-red divergences controlled by a high energy or ultra-violet cutoff (the bandwidth of the Kondo model), this indicates that intermediate states at arbitrarily high energies are involved in low energy processes in an essential way. This suggests the idea of exorcising the divergences progressively by truncating the Hilbert space, removing these high energy states a few at a time and incorporating their effects in the renormalised coupling constants of an effective Hamiltonian that acts in the residual Hilbert space.

Exact transformations can be defined, yielding effective Hamiltonians in the reduced Hilbert space; since such transformations can only be formal simplifications of the problem, a price has to be paid: effective couplings are retarded (i.e., energy dependent) and new types of couplings are also generated. A simple example is the formal diagonalisation procedure:

$$\det\begin{bmatrix} \omega - H_0 & V^\dagger \\ V & \omega - H_1 \end{bmatrix} = \det\left(\omega - H_0^{\mathrm{eff}}(\omega)\right) \qquad (6.1.1)$$

where

$$H_0^{\mathrm{eff}}(\omega) = H_0 + V^\dagger(\omega - H_1)^{-1}V \qquad (6.1.2)$$

which acts in the subspace of H_0.

In general such transformations are formal devices, devoid of any physical content. However, in the case where perturbation theory in the original coupling constant is infra-red divergent, it is likely that the new types of interactions generated by the scaling transformations

are, in the RG jargon, 'irrelevant', in that they are dominated by the coupling giving rise to the divergent processes, and may be ignored. As an infra-red divergence is at the heart of the problem, the ω-dependence of the renormalised dominant coupling may also be ignored, and the $\omega=0$ values concentrated on.

In these circumstances, the Hamiltonian has a scaling property under such a renormalisation procedure. The effective Hamiltonian generated is of the same form as the original, but with different values of the cutoff and coupling constants. Thus the renormalisation transformation shows that a family of Hamiltonians of the original form, lying along a trajectory in the parameter space of coupling constants of the model, are in fact equivalent, at least in those properties of the weak-coupling, long-time, low energy limit associated with the divergence of perturbation theory. As the cutoff is reduced, the effective Hamiltonian moves along this trajectory in parameter space, hence the term 'scaling': the problem has been scaled to a'different' but physically equivalent one.

Such scaling behaviour implies that the properties of the Hamiltonian in an N-dimensional parameter space (excluding the cutoff parameter, so that there are in fact N+1 apparent parameters of the theory) may be expressed in terms of the N scaling invariants, the N independent functions of the N coupling constants plus the cutoff that remain invariant under scaling, and define the trajectories.

Scaling tractories begin or end at 'fixed points' of the transformation in parameter space. The model around which perturbation theory is divergent will be one such fixed point. Fixed points are either stable or unstable depending on whether the model moves away or towards them as the cutoff is reduced (Fig. (6.1)). More complicated structures

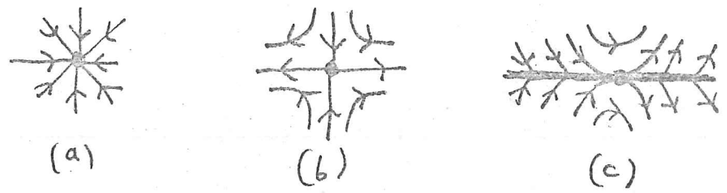


Fig. (6.1) (a) Stable fixed point; (b) unstable fixed point; (c) line of fixed points, stable at left.

such as lines of fixed points, etc. are possible. Detailed accounts of renormalisation group theory, mainly applied to critical phenomena, are given in the books by Ma (1976) and Toulouse (1977).

Scaling equations may be developed analytically as power series expansions in the dominant coupling, which vanishes at the fixed point. They will only be valid in the immediate vicinity of the fixed point in parameter space, where the divergent coupling dominates the physical properties. They may be integrated to find the form of the scaling invariants in the neighbourhood of the fixed point. These will in general be non-analytic functions of the coupling constant, which is why perturbation theory is divergent in the first place. As the validity of the scaling equations is restricted to the weak-coupling limit only the non-analytic part of these invariants will in general be obtainable by these techniques.

It is useful to summarise what can and what cannot be achieved using these types of scaling theories, based on power series or diagrammatic expansions of the scaling equations around the weak coupling limit.

(A). What is possible.

(1) Extraction of the non-analytic form of the N scaling invariants that characterise the (N parameter + cutoff) problem.

(2) Identification of 'phase transitions' in parameter space - surfaces dividing the space into regions scaling to ('in the domain of') different stable fixed points. These are associated with unstable fixed points (Fig.(6.1(b))): the power series expansion of the scaling equations allows identification of these 'phase boundaries' only in the vicinity of an unstable fixed point.

(3) Scaling to an exactly soluble model, provided it is close enough to the fixed point to be within the range of validity of the scaling equations. This proviso makes this a case of very limited applicability.

(B) What is not possible.

(1) Scaling far enough away from the fixed point that the coupling constant becomes large enough so the problem is quantitatively treatable by some other method (e.g., by an expansion in 1/(coupling constant)).

(2) Scaling to an "exactly soluble" model that does not lie close to the fixed point.

The reason that these approaches can not be made to work quantitatively is that as the scaling trajectory leaves the immediate vicinity of the weak coupling fixed point, the inevitable "irrelevant" couplings grow, and become of equal importance as the relevant ones; as such irrelevant couplings are inherently untreatable at intermediate coupling strengths, quantitative connection of the two limits is not possible . Both these two objectives were goals of the original of the original scaling theories of the Kondo model; it was hoped that by obtaining enough terms of the scaling equations expansion, that (2) at least could be realised, as an "exactly soluble" (exact in an asymptotic sense) model was tantalisingly available at intermediate coupling strength (Toulouse (1969)).

It turns out that the scaling equation expansion can only be unambiguously derived as far as necessary for obtaining the leading non-analytic behaviour of the scaling invariants. The higher order terms have coefficients that depend on the structure of the cutoff, and hence lack the "universality" or "scaling" property that allows the cutoff to be characterised by a single scale parameter. The attempt to obtain higher order terms (e.g., Armytage (1973)) has thus not turned out to be fruitful.

In the following sections, it will be stressed that all information available to characterise the universal weak coupling behaviour will be extracted from the lowest order term of the scaling equation expansion (or lowest two terms in marginal cases like the isotropic Kondo model).

The scaling theory of the Kondo model was first introduced by Anderson, Yuval and Hamann (1970). They separated the exchange interaction into spin flipping and spin conserving parts, thus considering a generalised problem with an anisotropic exchange interaction. An asymptotically exact expansion of the partition function was developed in powers of the spin flipping term, the spin conserving term being treated exactly. Scaling equations were then derived by studying the effect of reducing the bandwidth cutoff. A similar application of this so-called "space-time" technique to the screened asymmetric Anderson model, using the partition function expansion (5.5.3,14), will be described here.

A second version of the scaling theory, the so-called "poor man's" approach, was introduced by Anderson (1970). This is more similar to the field-theoretic approach, as it is based on a diagrammatic expansion, but still has significant conceptual differences with such approaches. In this technique, both spin-flip and spin-conserving processes are treated perturbatively, and thus on an equal footing. In many ways this is a superior formulation of the scaling technique, being "cleaner" and more easily generalised, and

providing certain terms not directly obtainable by the "space-time" technique; however both methods have their merits: the "space-time" technique allows the complete summation of certain classes of terms such as the spin-conserving processes which are treated exactly. An alternative derivation of the scaling equations for the asymmetric Anderson model, using a technique related to the "poor man's" approach, will also be presented.

A third type of treatment, the numerical renormalisation group technique of Wilson (1975), has eventually proved most successful in quantitatively studying the crossover from high temperature to low temperature behaviour. It is not based on expansions in the coupling, and is thus not restricted to studying properties near the fixed points. It works with numerical representations of the effective Hamiltonian as very large matrices, and is thus able to quantitatively take account of many of the "irrelevant" couplings that are important at intermediate coupling strength, where there is no simple representation of the effective Hamiltonian. Being numerical, such results are not as enlightening as those obtained from analytical techniques, and this method should perhaps be resorted to for providing precise numerical connection across the intractable crossover regimes between simple limiting fixed points that have first been explored qualitatively by one of the analytical scaling techniques.

As an example of the "space-time" technique, a simpler model, the resonant-level model, with coupling to Tomonaga bosons, is treated in the next section. This model turns out to be isomorphic to the anisotropic Kondo model originally discussed by Anderson, Yuval and Hamann (1970).

6.2 The Resonant Level Model with Boson Coupling

The resonant level model (Toulouse (1969)) is the spinless analogue of the Anderson model, with an impurity level right at the Fermi level.

$$H = \sum_k \varepsilon_k c_k^\dagger c_k + \sum_k V_{kd} c_k^\dagger c_d + E c_d^\dagger c_d \qquad (6.2.1)$$

The term E may be regarded as a coupling to an external field, the analogue of a magnetic field. This model is of course diagonalisable and exactly soluble. For the case $\Delta(\omega)$ constant, T = 0, the static susceptibility χ_E is $(\pi\Delta)^{-1}$.

Coupling to a boson field may be considered:

$$H' = \sum_q \omega_q b_q^\dagger b_q + g n_d \sum_q \kappa_q b_q + h.c. \qquad (6.2.2)$$

By second order perturbation theory in g:

$$\chi_E = \frac{1}{\pi\Delta}\left(1 + g^2 \int_0^\infty \frac{f(\omega)}{\omega^2+\Delta^2} d\omega + O(g^4)\right) \qquad (6.2.3)$$

$$f(\omega) = \sum_q |\kappa_q|^2 \delta(\omega - \omega_q) \qquad (6.2.4)$$

Unless the boson spectrum is phonon-like (i.e., Lim $\omega\to 0$ $f(\omega)/\omega \to 0$), perturbation theory is term by term divergent in the $\Delta\to 0$ limit. Using the type of partition function expansion in Δ derived in the last chapter, the small Δ, finite g, problem can be treated by the scaling theory technique ('space-time' version) introduced by Anderson and Yuval for the Kondo problem (Anderson, Yuval and Hamann (1970)). Since this includes the g = 0 problem as a special case, (6.2.3) will provide a useful check on the results.

As seen in the previous chapter, in the $\Delta \ll \omega_D$ (= Debye temperature) limit, a phonon-like boson field merely renormalises the hybridisation parameter Δ by a factor of the square of the overlap between the two relevant displaced coherent phonon fields.

$$\Delta^{eff} = \Delta \exp - g^2 \int_0^\infty d\omega \frac{f(\omega)}{\omega^2} \; ; \qquad (6.2.5)$$

hence

$$\lim_{\Delta\to 0} \chi_E = \frac{1}{\pi\Delta} \exp g^2 \int_0^\infty d\omega \frac{f(\omega)}{\omega^2} \qquad (6.2.6)$$

Expanding the exponential in powers of g^2, (6.2.6) is seen to agree with the $\Delta \to 0$ limit of perturbation theory in g (6.2.3). In general, the argument of the exponential may be large, and (6.2.6) represents summation to infinite order of the leading terms of perturbation theory in g as $\Delta \to 0$.

For a Tomonaga-type boson field,

$$\lim_{\Delta\to 0} g^2 \int_0^\infty d\omega \frac{f(\omega)}{\omega^2+\Delta^2} = -\varepsilon \ln(\Delta/W) \; , \qquad (6.2.7)$$

where W is a cutoff of the order of the bandwidth of the conduction band the 'Tomonagons' were derived from.

The partition function expansion of (6.2.1) in powers of the hybridisation Δ is a special case of (5.5.10), with $E_\downarrow = \infty$, $E_\uparrow = E$, and U = 0.

$$\frac{Z}{Z_0} = \sum_N (\beta^2 \Delta W)^N \int_0^1 dx_{2N} \cdots \int_{x_{2N-1}}^{x_2} dx_1 \exp - \{\}$$

$$(x_{2N} > x_{2N-1} \cdots > x_1 > x_{2N-1})$$

$$\{\} = \{\beta E \sum_L (-1)^L x_L - (1+\varepsilon) \sum_{(-)} (-1)^{(-)} \ln^* \beta W \sin \pi |x_L - x_J|\} \qquad (6.2.8)$$

The cutoff in the logarithm may be characterised more explicitly:

$$\ln^* X \equiv \ln f(x)$$

$$f(x) = x \quad (x >> 1)$$

$$= 1 \quad (x << 1) \qquad (6.2.9)$$

The cutoff region is best described by the function g(x):

$$g(x) = 1 - x f'(x)/f(x) \quad . \tag{6.2.10}$$

which is of order unity inside the cutoff region, and zero outside it (Fig. (6.1)).

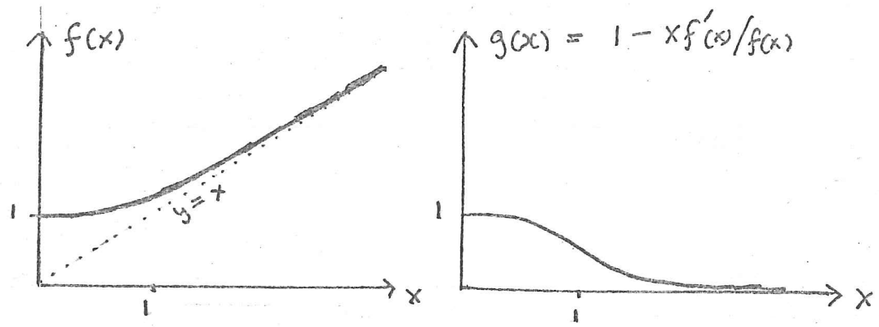


Fig. (6.1). Form of the cutoff functions f(x) and g(x).

In particular, for λ infinitesimal:

$$\ln^*((1+\lambda)x) = \ln(f(x)) + \lambda x f'(x)/f(x)$$

$$= \ln^*(x) + \lambda - \lambda g(x) \tag{6.2.11}$$

By such a transformation, the problem can be related to a new problem where W is replaced by W' = (1-λ)W:

$$\frac{Z}{Z_0} = \sum_N (\beta^2 \Delta W)^N \int dx_i \cdots \exp - \left[\beta E \sum_i (-1)^i x_i - (1+\varepsilon) \sum_{i>j} (-1)^{i-j} \ln^*(\beta W (1-\lambda) \sin\pi |x_i - x_j|)\right]$$

$$\times \left\{ \exp\left(\lambda (1+\varepsilon) \sum_{i>j} (-1)^{i-j}\right) \exp -\lambda (1+\varepsilon) \sum_{i>j} (-1)^{i-j} g(\beta W \sin\pi |x_i - x_j|) \right\} \tag{6.2.13}$$

The first factor in the correction factor in curly brackets reduces to $(1-\lambda(1+\varepsilon))^N$ and renormalises $(\beta^2 \Delta W)$; the second factor leads to a correction term given by a sum over all configurations $(x_1,..,x_{2N})$ subject to the restriction that one pair (x_i,x_j) have a separation inside the range of the cutoff function g(x). Expanding the exponential to first

order in λ, the correction factor in (6.2.13) becomes:

$$\{\} = \left\{(1-\lambda(1+\varepsilon))^N \left[1 - \lambda(1+\varepsilon) \sum_{i>j} (-1)^{i-j} g(\beta W \sin\pi (x_i - x_j))\right]\right\} \tag{6.2.14}$$

For βW large, g($\beta W \sin x$) is infinitesimal except at very small x, so $\sin\pi x$ can be linearised. Integrating out the restricted pair of variables (x_i,x_j) in a configurational term of order N leads to a correction of order N-1; the dominant corrections of order N come from configurations of order N+1 with the extra pair (x_i,x_j) having a spacing within the cutoff. Such corrections may be systematically generated by adding such a closely spaced pair to the configuration $(x_1,..,x_{2N})$ in all possible ways, and then integrating it out . This generates all corrections where $|i-j| = 1$. Higher order corrections come from $|i-j| = 2,3$ etc. These terms may be neglected in the weak hybridistion limit. Figure (6.2) shows the corrections graphically. A configuration is depicted by a graph showing the

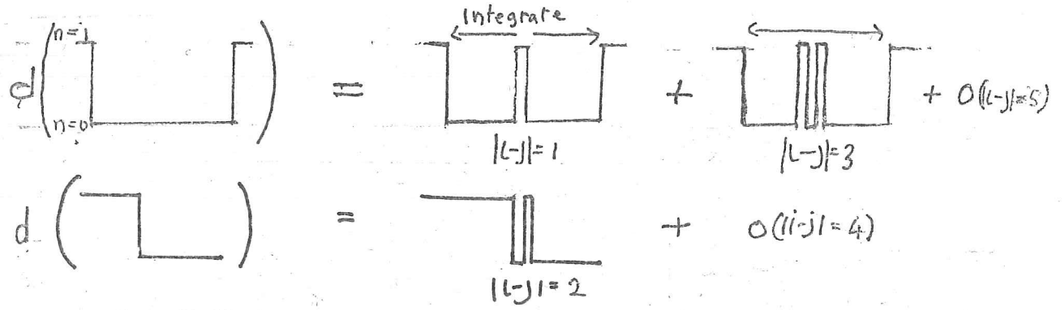


Fig. (6.2). Correction terms due to scaling cutoff.

occupation of the d-orbital as a function of imaginary time.

The $|i-j| = 1$ corrections depend on a single aspect of the cutoff function g(x), essentially its range; in these terms the cutoff can be described by a <u>single</u> parameter, while higher order terms will involve more details of the cutoff region, and thus lie outside the validity of the asymptotic approximation. The 'universal' aspects of the behaviour in

the weak hybridisation limit must therefore be given by the $|i-j| = 1$ terms alone, and henceforth only these will be considered.

The partition function expansion (6.2.13) may be rewritten:

$$\frac{Z}{Z_0} = \sum_N \left(\beta^2\Delta W(1-\lambda(1+\varepsilon))\right)^N \int_i^{2N} dx_i \exp -\left(\beta E\sum_i (-1)^i x_i - (1+\varepsilon)\sum_{i>j}(-1)^{i-j} \ln^*(\beta W \sin\pi|x_i-x_j|)\right)$$
$$\times\left\{1 + \lambda(1+\varepsilon)\frac{\beta\Delta}{\pi}\sum_i \int_{x_i}^{x_{i+1}} dx \int_0^{(\infty)} dy\, g(y) \exp\left(\frac{-y}{\beta W\pi}\frac{d}{dx}[\ ]\right) + o(\lambda^2)\right\} \qquad (6.2.15)$$

where

$$[\ ] = \left[(-1)^i \beta E x + (1+\varepsilon)\sum_j (-1)^{i-j} \ln^*(\beta W \sin\pi|x-x_j|)\right] \times \exp -(1+\varepsilon)\ln f(y) \qquad (6.2.16)$$

Since $\ln f(y) \simeq 0$ inside the cutoff region, the last factor $\simeq 1$ and may be neglected. Expanding the exponential in $(y/\pi\beta W)$ and integrating:

$$\{\} \to 1 + \frac{\lambda}{\pi}(1+\varepsilon)\beta\Delta\int_0^\infty dy\, g(y) \quad -2\lambda(1+\varepsilon)\frac{\Delta}{\pi^2 W}\int_0^\infty y\, g(y)\, dy\ [\ ]$$

$$[\ ] = -\beta E\sum_i (-1)^i x_i + 2(1+\varepsilon)\sum_{i>j}(-1)^{(-)} \ln^*\beta W \sin\pi|x_i-x_j| \qquad (6.2.17)$$

since λ is infinitesimal

$$\{\} = \exp\left(\beta\lambda(1+\varepsilon)\Delta\cdot\left(\frac{1}{\pi^2}\int_0^\infty g(y)dy\right)\right)\cdot\exp\left(\lambda(1+\varepsilon)\frac{\Delta}{W}\left(\frac{2}{\pi^2}\int_0^\infty y g(y)dy\right)[\ ]\right) \qquad (6.2.18)$$

The correction factor has the effect of merely shifting the ground state energy, and renormalising the parameters of the initial partition function. No new types of interactions appear. This scaling of the problem to a problem of the same form but different parameters means that a whole class of such problems becomes identical when expressed in terms of some scaling parameters. For example, all weak coupling Kondo problems (a special case of the partition function (6.2.8) become identical when expressed in terms of the characteristic Kondo temperature T_K.

The cutoff parameter D, ($\simeq$ W) is defined by $D = \frac{1}{2}\pi^2 W\left(\int_0^\infty y g(y) dy\right)^{-1}$. Though of the order of magnitude of W, it is not the same parameter. W arises from the long-time asymptotic behaviour of the propagators, and is known exactly (cf. (6.2.7)). D describes the short-time

behaviour, and is only known within the accuracy of the asymptotic approximation. The problem has scaled so that

$$\frac{Z}{Z_0}(W, E, \varepsilon, \Delta) = e^{-\beta F'}\frac{Z}{Z_0}(W', E', \varepsilon', \Delta') \qquad (6.2.19)$$

$$F' = -\lambda(1+\varepsilon)\frac{\Delta}{D}\alpha \qquad (6.2.20)$$

(where α is an undetermined parameter of order unity)

$$\begin{aligned} E' &= E + \lambda(1+\varepsilon)\frac{\Delta}{D}E \\ \varepsilon' &= \varepsilon + 2\lambda(1+\varepsilon)^2\frac{\Delta}{D} \\ \Delta' &= \Delta - \lambda\varepsilon\Delta \\ D' &= D - \lambda D' \\ W' &= W - \lambda W' \end{aligned} \qquad (6.2.21)$$

These may be written as scaling equations.

$$\begin{aligned} \frac{dE}{d\ln D} &= (1+\varepsilon)\frac{\Delta}{D}\cdot E + o\left(\frac{\Delta}{D}\right)^2 \\ \frac{d\varepsilon}{d\ln D} &= 2(1+\varepsilon)^2\frac{\Delta}{D} + o\left(\frac{\Delta}{D}\right)^2 \\ \frac{d\Delta}{d\ln D} &= \varepsilon\Delta + o\left(\frac{\Delta^2}{D}\right) \end{aligned} \qquad (6.2.22)$$

These equations were first developed for the Kondo model (Anderson, Yuval and Hamann (1970)), generalised to anistropic coupling to the spin, ($J\vec{S}.\vec{S} \to J_z S_z S_z + \frac{1}{2}J_{\pm}(S^+S^- + S^-S^+)$. The correspondence to the Anderson-Yuval-Hamann equations, clarified by Armytage (1973), is

$$\begin{aligned} \frac{\Delta}{W} &\leftrightarrow \left(\frac{J_\pm\rho}{2}\right)^2\left(1-\frac{2}{\pi}\tan^{-1}\left(\frac{\pi J_z\rho}{4}\right)\right)^2 \simeq \left(\frac{J_\pm\rho}{2}\right)^2\left(1-\frac{J_z\rho}{2}\right)^2 \\ 1+\varepsilon &\leftrightarrow 2\left(1+\frac{2}{\pi}\tan^{-1}\left(\frac{\pi J_z\rho}{4}\right)\right)^2 \simeq 2\left(1+\frac{J_z\rho}{2}\right)^2 . \end{aligned} \qquad (6.2.23)$$

Translating (6.2.22) and expanding in powers of J

$$\begin{aligned} \frac{dJ_z\rho}{d\ln D} &= \bar{\alpha}\left((J_\pm\rho)^2 + \frac{1}{2}(J_z\rho)(J_\pm\rho)^2\right) + o(J\rho)^4 \\ \frac{dJ_\pm\rho}{d\ln D} &= (J_z\rho)(J_\pm\rho) + \frac{1}{4}(J_\pm\rho)(J_z\rho)^2 + \bar{\beta}(J_\pm\rho)^3 + o(J\rho)^4 \end{aligned} \qquad (6.2.24)$$

$\bar{\alpha}$ is the cutoff parameter W/D, and $\bar{\beta}$ is an undetermined parameter arising from $|i-j|=3$ terms in the expansion. In the isotropic Kondo problem, underlying Ward-like identities must preserve the symmetry $J_\pm = J_z$, even though this symmetry is no longer manifest in the

partition function (6.2.8). This allows the identification

$\bar{\alpha} = 1$, $\bar{\beta} = \frac{1}{4}(+O(J_z - J_\pm))$, so the two equations become identical, and for the isotropic Kondo model:

$$\frac{dJ\rho}{d\ln D} = (J\rho)^2 + \frac{1}{2}(J\rho)^3 + O(J\rho)^4 \qquad (6.2.25)$$

which as pointed out earlier is completely sufficient to determine the form of the universal parameter $T_K = D(|J\rho|)^{\frac{1}{2}}\exp(1/J\rho)$ in the weak-coupling limit.

For small Δ/W , the scaling equations (6.2.22) can be integrated; E=0 is a 'fixed point', and the 'scaling trajectories' in the $(\varepsilon, \Delta/D)$ plane are:

$$\frac{d\Delta/D}{d\varepsilon} = \frac{(\varepsilon - 1)}{2(1+\varepsilon)^2} + O(\Delta/D)$$

$$\rightarrow \frac{\Delta}{D} = \frac{1}{1+\varepsilon} + \frac{1}{2}\ln(|1+\varepsilon|) + \text{constant} \qquad (6.2.26)$$

The scaling trajectories as D decreases are shown in Fig. (6.3). $\Delta/D = 0$ is a line of fixed points, stable for $\varepsilon > 1$, unstable for $\varepsilon < 1$.

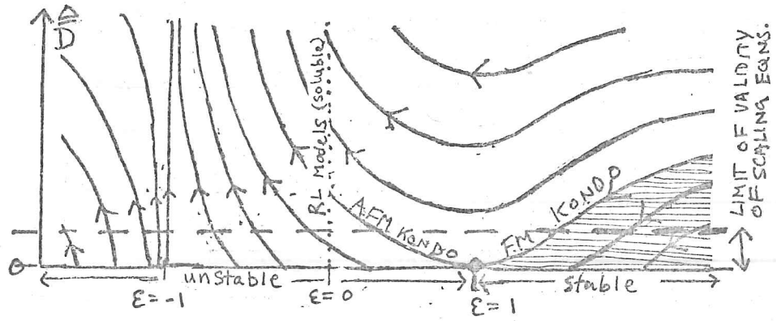


Fig. (6.3). Scaling trajectories in the $(\varepsilon, \Delta/D)$ plane as D is decreased. (E=0).

An important feature is the Kondo trajectory, going through the fixed point at $\Delta/D = 0$, $\varepsilon = 1$, which divides stable from unstable fixed points. This is the reason the Kondo model shows 'marginal' behaviour (in the jargon of RG theory (Wilson (1975)). The FM trajectory ends at the $\Delta/D = 0$ fixed point, but the AFM trajectory moves away, corresponding to a 'phase transition' at T = 0, J = 0. $\varepsilon = -1$ represents a trivially soluble model as the logarithmic terms vanish. The $\varepsilon = 0$ line is the line of soluble resonant level (RL) models, for which an exact solution

exists for finite Δ/D.

For ε small, positive, the trajectory passes through the line of RL models at $\varepsilon = 0$ while Δ/D is still small. It would seem at first sight that this is a case that can be solved by scaling to the RL model. If this program is naively carried out, using the lowest order terms of the scaling equations (6.2.22), and the trajectory shown in Fig. (6.4), an incorrect answer is

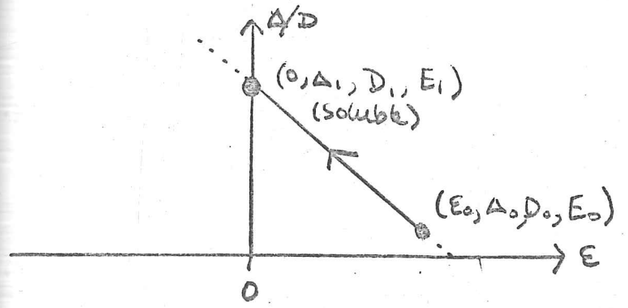


Fig. (6.4). Attempted solution of the ε small, positive problem by scaling to the soluble RL ($\varepsilon = 0$) model.

obtained. The reason for this can be seen by examining the undetermined higher order terms of the scaling equations: over much of the trajectory Δ/D is of the same order of magnitude as ε, and it is inconsistent to neglect terms of order $(\Delta/D)^2$ while retaining those of order $(\varepsilon\Delta/D^2)$ - yet if all such terms are neglected, the scaling equations assume their $\varepsilon = 0$ form and the scaling program cannot be carried out.

Although scaling to the RL model is thus not possible, scaling invariants (similar to T_K for the Kondo model) can be identified in the weak hybridisation limit. For $\Delta/D \ll 1$, $d\varepsilon/d(\ln D) \simeq 0$ and ε is one of the scaling invariants. The other scaling equation $d\Delta/d(\ln D) = \varepsilon\Delta$ can then be integrated to give Δ/D^{ε} as another invariant. Taking a combination of the two with the dimensions of energy, the most convenient choice

for the second invariant is $\Delta^*(\Delta,\varepsilon,D) = \Delta(\Delta/D)^{\varepsilon/1-\varepsilon}$.

Physical properties of the model, which has three parameters Δ, D, and ε, can, in the $\Delta/D \ll 1$ limit, be expressed solely in terms of the two invariants Δ^* and ε. In particular, on dimensional grounds, the zero temperature susceptibility must be given by

$$\chi(T=0) = F(\varepsilon)/\Delta^* \qquad (6.2.27)$$

where $F(\varepsilon)$ is an unknown function of ε. For $\varepsilon < 1$ the scaling trajectories show continuity of behaviour. The unknown function $F(\varepsilon)$ is thus analytic, and can be expanded as a power series in ε. For $\varepsilon=0$, $\chi(T=0) = (\pi\Delta^*)^{-1}$, so for $\varepsilon \gtrsim 0$:

$$\chi(T=0) \simeq \frac{1}{\pi\Delta}\left(\frac{\Delta}{D}\right)^{-\varepsilon} = \frac{1}{\pi\Delta}\exp -\varepsilon \ln(\Delta/D) \quad . \qquad (6.2.28)$$

The precise value of D can be obtained through comparison with perturbation theory in g: from (6.2.7)

$$-\varepsilon \ln(\Delta/D) = \lim_{\Delta\to 0} g^2 \int_0^\infty d\omega\, f(\omega)/(\omega^2+\Delta^2) \quad . \qquad (6.2.29)$$

and, as in the 'phonon' case,

$$\lim_{\Delta\to 0} \chi(T=0) = \frac{1}{\pi\Delta}\exp g^2 \int_0^\infty d\omega \frac{f(\omega)}{\omega^2+\Delta^2} \qquad (0 \le \varepsilon \ll 1) \quad . \qquad (6.2.30)$$

A description of the temperature dependence of physical properties may also be deduced from the scaling theory. At finite temperatures, the scaling equations are only valid when the effective bandwidth D is larger than T. The equilibrium properties of the system at temperature T are determined by real physical processes involving conduction band states with energies of order T. Higher energy conduction band states are only excited in virtual processes, and hence their only effect is to renormalise the low energy effective couplings. Thus thermodynamic properties of the system may be described in terms of temperature dependent effective couplings defined by using the scaling equations to scale the bandwidth down to T. In the problem at hand, this gives a temperature dependent $\Delta^{eff}(T)$:

$$\Delta^{eff}(T) = \Delta\left(\frac{T}{D}\right)^{\varepsilon} \quad . \qquad (6.2.31)$$

As the temperature is reduced, $\Delta^{eff}(T)$ changes. At high T, the physics is controlled by T, and Δ^{eff} is irrelevant. Δ^* has a simple interpretation as the crossover temperature $T = \Delta^{eff}(T) = \Delta^*$ below which the thermal fluctuations become irrelevant compared to those induced by the hybridisation. Below the crossover there is no further renormalisation, and $\Delta^{eff}(T) = \Delta^*$ is constant; properties in this low temperature regime are essentially temperature independent. This scaling process and eventual crossover as a function of temperature is shown in Fig. (6.5). The crossover temperature goes to zero as ε goes to 1;

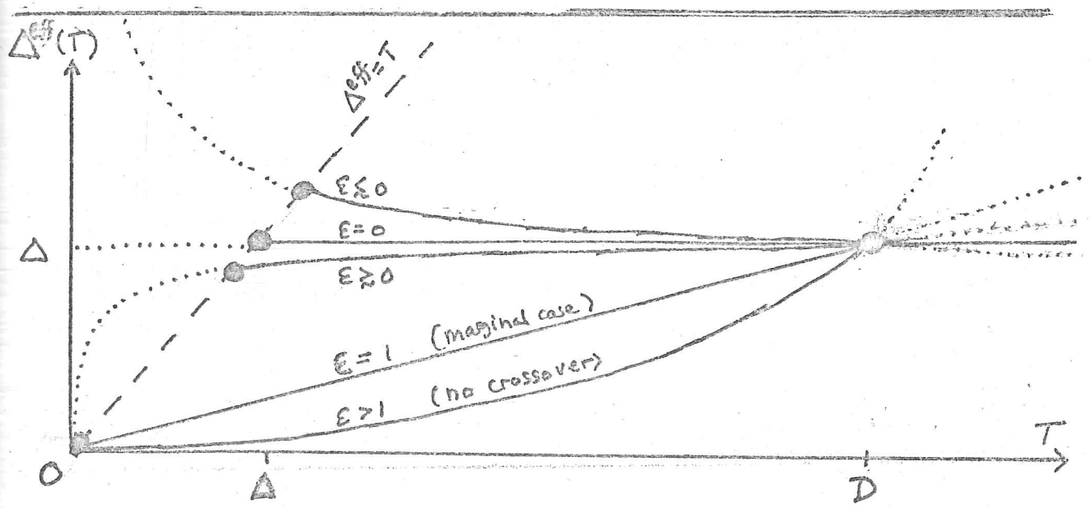


Fig. (6.5). Renormalisation of Δ^{eff} in the temperature range $\Delta^* < T < D$, where Δ^* is the crossover temperature where $\Delta^{eff}(T) = T$.

for $\varepsilon > 1$, there is no crossover and $\Delta^{eff}/D \to 0$ as $T \to 0$, so the susceptibility diverges as T^{-1} with the same coefficient as the free orbital ($\Delta = 0$). This may be seen more clearly by noting that the high temperature ($T \gg \Delta^{eff}$) expansion for the susceptibility derived from the partition function (6.2.8) will take the form

$$\chi \propto \frac{1}{T}\left(1 - \text{Constant.}\ \frac{\Delta^{eff}}{T} \ldots\right) \quad . \qquad (6.2.32)$$

for the second invariant is $\Delta^*(\Delta,\varepsilon,D) = \Delta(\Delta/D)^{\varepsilon/1-\varepsilon}$.

Physical properties of the model, which has three parameters Δ, D, and ε, can, in the $\Delta/D \ll 1$ limit, be expressed solely in terms of the two invariants Δ^* and ε. In particular, on dimensional grounds, the zero temperature susceptibility must be given by

$$\chi(T=0) = F(\varepsilon)/\Delta^* \qquad (6.2.27)$$

where $F(\varepsilon)$ is an unknown function of ε. For $\varepsilon < 1$ the scaling trajectories show continuity of behaviour. The unknown function $F(\varepsilon)$ is thus analytic, and can be expanded as a power series in ε. For $\varepsilon=0$, $\chi(T=0) = (\pi\Delta^*)^{-1}$, so for $\varepsilon \gtrsim 0$:

$$\chi(T=0) \simeq \frac{1}{\pi\Delta}\left(\frac{\Delta}{D}\right)^{-\varepsilon} = \frac{1}{\pi\Delta}\exp -\varepsilon \ln(\Delta/D) \quad . \qquad (6.2.28)$$

The precise value of D can be obtained through comparison with perturbation theory in g: from (6.2.7)

$$-\varepsilon \ln(\Delta/D) = \lim_{\Delta\to 0} g^2 \int_0^\infty d\omega\, f(\omega)/(\omega^2+\Delta^2) \quad . \qquad (6.2.29)$$

and, as in the 'phonon' case,

$$\lim_{\Delta\to 0} \chi(T=0) = \frac{1}{\pi\Delta}\exp g^2 \int_0^\infty d\omega \frac{f(\omega)}{\omega^2+\Delta^2} \qquad (0 \le \varepsilon < 1) \quad . \qquad (6.2.30)$$

A description of the temperature dependence of physical properties may also be deduced from the scaling theory. At finite temperatures, the scaling equations are only valid when the effective bandwidth D is larger than T. The equilibrium properties of the system at temperature T are determined by real physical processes involving conduction band states with energies of order T. Higher energy conduction band states are only excited in virtual processes, and hence their only effect is to renormalise the low energy effective couplings. Thus thermodynamic properties of the system may be described in terms of temperature dependent effective couplings defined by using the scaling equations to scale the bandwidth down to T. In the problem at hand, this gives a temperature dependent $\Delta^{eff}(T)$:

$$\Delta^{eff}(T) = \Delta\left(\frac{T}{D}\right)^{\varepsilon} \quad . \qquad (6.2.31)$$

As the temperature is reduced, $\Delta^{eff}(T)$ changes. At high T, the physics is controlled by T, and Δ^{eff} is irrelevant. Δ^* has a simple interpretation as the crossover temperature $T = \Delta^{eff}(T) = \Delta^*$ below which the thermal fluctuations become irrelevant compared to those induced by the hybridisation. Below the crossover there is no further renormalisation, and $\Delta^{eff}(T) = \Delta^*$ is constant; properties in this low temperature regime are essentially temperature independent. This scaling process and eventual crossover as a function of temperature is shown in Fig. (6.5). The crossover temperature goes to zero as ε goes to 1;

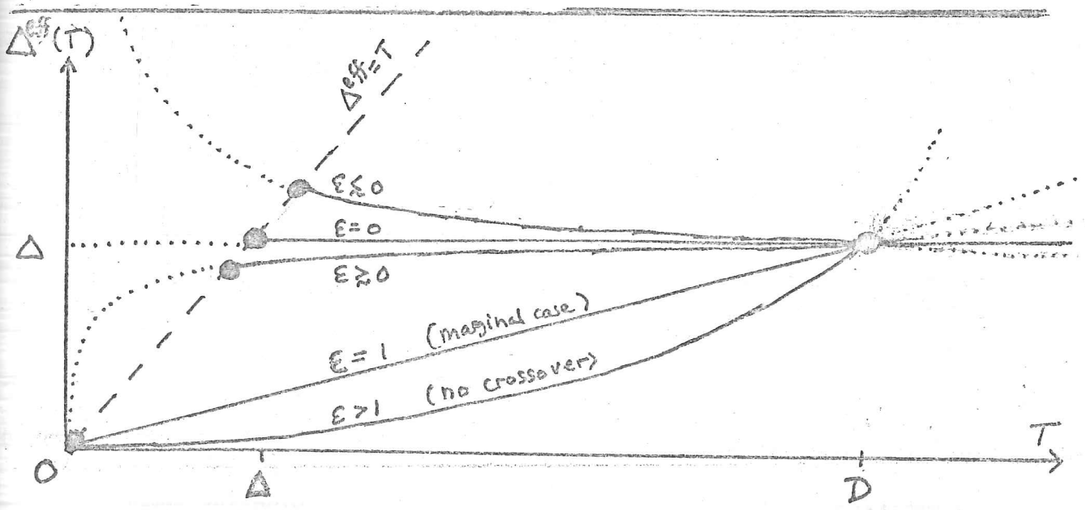


Fig. (6.5). Renormalisation of Δ^{eff} in the temperature range $\Delta^* < T < D$, where Δ^* is the crossover temperature where $\Delta^{eff}(T) = T$.

for $\varepsilon > 1$, there is no crossover and $\Delta^{eff}/D \to 0$ as $T \to 0$, so the susceptibility diverges as T^{-1} with the same coefficient as the free orbital ($\Delta = 0$). This may be seen more clearly by noting that the high temperature ($T \gg \Delta^{eff}$) expansion for the susceptibility derived from the partition function (6.2.8) will take the form

$$\chi \propto \frac{1}{T}\left(1 - \text{Constant.}\ \frac{\Delta^{eff}}{T} \ldots\right) \qquad (6.2.32)$$

The correction term vanishes as $T \to 0$ when $\varepsilon > 1$. In the marginal caee $\varepsilon = 1$, the correction term stays constant, implying a Curie law with a reduced coefficient; however the higher order terms of the scaling equations eventually cause Δ/D to increase, as can be seen from the scaling trajectories in Fig.(6.3), and this Curie law is quenched below some characteristic temperature that vanishes exponentially as Δ/D goes to zero.

Finally, the problem of the RL model coupled to Tomonaga-bosons can be put in the context of the family of models where the boson spectral density $f(\omega) \sim \omega^d$ as $\omega \to 0$. For $d > 1$, the small Δ limit becomes a renormalised (unscreened) RL model. $d = 1$ is the Tomonaga case treated above. For $d < 1$, the boson propagators dominate the long time behaviour, with an $x^{-(1+d)}$ dependence. The system will order (i.e., $\chi \to \infty$) below some finite temperature T_c. As $d \to 1$, $T_c \to 0$, and at $d = 1$, whether or not the system orders depends on the coupling constant ε. As $d \to 0$, $T_c \to \infty$, the effective level shift C ($= \int_0^\infty d\omega f(\omega)/\omega$) diverges, and mean-field theory becomes exact. $T_c(d)$ is shown schematically in Fig. (6.6).

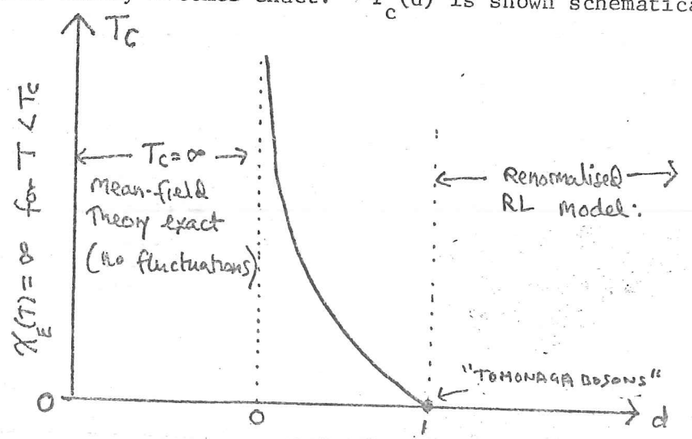


Fig. (6.6). (Schematic.) 'Ordering temperature' T_c, below which $\chi = \infty$, as a function of the boson infra-red exponent d. ($f(\omega) \sim \omega^d$).

6.3 Scaling Equations for the Asymmetric Regime of the Anderson Model

The scaling procedures just described will now be applied to the asymmetric regime of the Anderson model. Recalling (5.5.14), the partition function is given by

$$\frac{Z}{Z_0} = \sum_N (\beta^2 W\Delta)^N \int_0^1 dx_{2N} \cdots \int_{x_{2N-1}}^{x_2} dx_1 \sum_{\sigma_1 \cdots \sigma_{2N}} \left(\prod_i \delta_{\sigma_{2i}\sigma_{2i-1}} \right) \exp -\{\}$$

$$\{\} = \sum_i (-1)^i \beta E_{\sigma_i} x_i - \sum_{i>j} (\varepsilon + \gamma\delta_{\sigma_i\sigma_j})(-1)^{i-j} \ln^* \beta W \sin\pi|x_i - x_j| \qquad (6.3.1)$$

where $\gamma = 1$. Again writing

$$\ln^* \beta W \sin\pi|x| = \ln^* \beta W(1+\lambda)\sin\pi|x| - \lambda + \lambda\, g(\beta W \pi |x|) \qquad (6.3.2)$$

and using

$$\sum_{i>j} (-1)^{i-j} (\varepsilon + \gamma\delta_{\sigma_i\sigma_j}) = -(\varepsilon+\gamma)N \qquad (6.3.3)$$

the partition function becomes

$$\frac{Z}{Z_0} = \sum_N \left(\beta^2 W(1+\lambda)\Delta(1+\lambda(\varepsilon+\gamma-1))\right)^N \exp -\{\}$$

$$\times \left(1 + \lambda \sum_{i>j} (\varepsilon + \gamma\delta_{\sigma_i\sigma_j})(-1)^{i-j} g(\beta W \pi |x_i - x_j|)\right) \qquad (6.3.4)$$

As before, the dominant correction terms come from adding pairs with $|i-j| = 1$, and now $\sigma_i = \sigma_j$. This can be done in four ways (Fig. (6.7)):

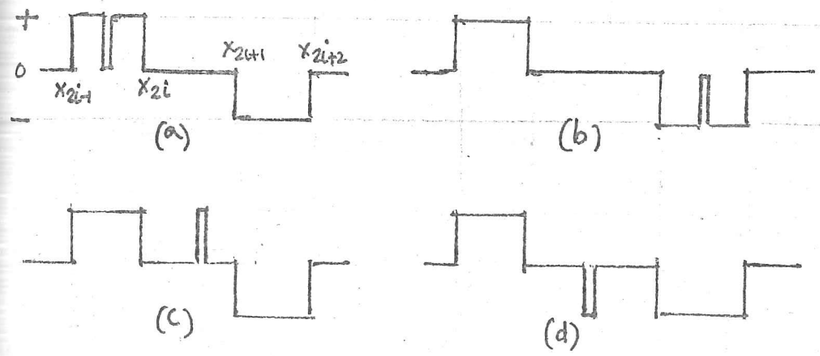


Fig. (6.7). The four types of $|i-j| = 1$ correction terms generated by scaling.

The correction factor becomes

$$1 - (\beta^2 \Delta W)\lambda(\varepsilon+\gamma) \sum_\sigma \left(\sum_{i\ \text{even}} + \sum_{i\ \text{odd}} \delta_{\sigma\sigma_i} \right) \int_{x_L}^{x_{L+1}(\infty)} dx \int_0^\infty \frac{dy}{\beta\pi W} g(y) \exp \frac{y}{\beta\pi W} \frac{d}{dx} [\ ]$$

$$[\ ] = -\beta(E + \sigma H)(-1)^i x + \sum_j (\varepsilon + \gamma\delta_{\sigma\sigma_j})(-1)^{i-j} \ln^* \beta\pi \sin|x_i - x_j| \qquad (6.3.5)$$

Repeating the manipulations of the previous section, the correction factor becomes:

$$\exp 2\beta\lambda(\varepsilon+\gamma) \triangleq \frac{\omega}{\pi}\int_0^\omega g(y)\,dy$$
$$\times \exp+\beta\lambda(\varepsilon+\gamma)\frac{\Delta}{\pi^2 W}\left(-\pi W\int_0^\omega g(y)\,dy + 3E\int_0^\omega g(y)\,y\,dy\right)\sum_i(-1)^i\chi_i$$
$$\times \exp+\beta\lambda(\varepsilon+\gamma)\frac{\Delta}{\pi^2 W}\left(-H\int_0^\omega g(y)\,y\,dy\right)\sum_i(-1)^i\sigma_i\chi_i$$
$$\times \exp\lambda(\varepsilon+\gamma)\frac{\Delta}{\pi^2 W}\left(\int_0^\omega y\,g(y)\,dy\right)\cdot\left(2\sum_{i>j}\left((3\varepsilon+\gamma)+\gamma\delta_{\sigma(i)\sigma(j)}\right)(-1)^{(i-j)}\ln^*\beta W|\sin\pi(\chi_i-\chi_j)|\right) \tag{6.3.6}$$

On replacing this correction factor (6.3.6) in the expression (6.3.4) for Z, a new Z of the same form as before (except for a ground state energy shift) is obtained. The transformation is

$$\begin{aligned}
W' &\to W + \lambda W\\
\Delta' &\to \Delta + \lambda(\varepsilon+\gamma-1)\Delta\\
\varepsilon' &\to \varepsilon + 2\lambda\frac{\Delta}{W}\left(\frac{1}{\pi^2}\int_0^\omega y\,g(y)\,dy\right)(\varepsilon+\gamma)(3\varepsilon+\gamma)\\
\gamma' &\to \gamma + 2\lambda\frac{\Delta}{W}\left(\frac{1}{\pi^2}\int_0^\omega y\,g(y)\,dy\right)(\varepsilon+\gamma)\gamma\\
E' &\to E - \lambda(\varepsilon+\gamma)\frac{\Delta}{W}\left(-3E\frac{1}{\pi^2}\int_0^\omega y\,g(y)\,dy + \frac{W}{\pi}\int_0^\omega g(y)\,dy\right)\\
H' &\to H + \lambda(\varepsilon+\gamma)\frac{\Delta}{W}\left(H\frac{1}{\pi^2}\int_0^\omega y\,g(y)\,dy\right).
\end{aligned} \tag{6.3.7}$$

and the scaling equations are

$$\begin{aligned}
\frac{d\Delta}{d\ln D} &= (\varepsilon+\gamma-1)\Delta\\
\frac{d\varepsilon}{d\ln D} &= \frac{\Delta}{D}(\varepsilon+\gamma)(3\varepsilon+\gamma)\ ;\ \frac{d\gamma}{d\ln D} = \frac{\Delta}{D}(\varepsilon+\gamma)\gamma\\
\frac{dE}{d\ln D} &= -\alpha(\varepsilon+\gamma)\frac{\Delta}{\pi} + \frac{3}{2}(\varepsilon+\gamma)\frac{\Delta}{D}E\ ;\ \frac{dH}{d\ln D} = \frac{1}{2}(\varepsilon+\gamma)\frac{\Delta}{D}H\ .
\end{aligned} \tag{6.3.8}$$

where α is an undetermined factor of order unity, arising from the precise structure of $g(x)$: $\alpha = \int_0^\omega g(y)\,dy$.

For $\varepsilon+\gamma<2$, the $\Delta/D = 0$ fixed point is unstable and reducing D results in scaling to larger Δ/D. Since initially $\gamma=1$, and the X-ray exponent ε is strictly limited by the Friedel sum rule to $-1<\varepsilon<1$, the initial values $\varepsilon+\gamma$ satisfy $2>\varepsilon+\gamma>0$; subsequent scaling may be seen from (6.3.8) to reduce $\varepsilon+\gamma$ even more below the upper limit of 2.

Scaling is thus always away from the $\Delta/D = 0$ fixed point.

In the limit $\Delta \ll D$, ε and γ are not renormalised, and the scaling equations (6.3.8) become:

$$\frac{d\varepsilon}{d\ln D}=0 \qquad \frac{d\gamma}{d\ln D}=0 \qquad \frac{dH}{d\ln D}=0 \tag{6.3.9}$$

$$\frac{d\Delta}{d\ln D} = \varepsilon\Delta \tag{6.3.10}$$

$$\frac{dE}{d\ln D} = -\tilde{\alpha}(\varepsilon)\frac{\Delta}{\pi} \tag{6.3.11}$$

$\tilde{\alpha}(\varepsilon)$ is a postive constant of order unity that cannot be obtained within the "space-time" scaling method. Note the new behaviour of these scaling equations compared to those of the resonant level model (6.2.22): the level parameter E is strongly scaled upwards as the bandwidth is reduced.

The occurence of an important undetermined constant in (6.3.11) is unsatisfactory; fortunately this problem can be resolved using the alternative "poor man's" approach to derive the scaling equations.

The effect of states near the high energy cutoff is mainly to renormalise the bare states $|0\rangle$ and $|1\sigma\rangle$ of the impurity orbital. If the cutoff is reduced this renormalisation must be taken into account. Suppose that $\Delta(\omega) \simeq 0$ except in the cutoff region $|\omega| \simeq D$ and $\Delta(\omega)=0$. The scaling procedure is to divide $\Delta(\omega)$ into $[\Delta((1+\lambda)\omega)] - [\lambda\omega\Delta'(\omega)]$, where λ is positive and infinitesimal. The second term $-\lambda\omega\Delta'(\omega)$ (which is positive) is that part of the spectral density $\Delta(\omega)$ representing those high energy particle and hole states that are to be integrated out, leaving a residual spectral density $\Delta((1+\lambda)\omega)$ of the same <u>form</u>, but reduced in <u>scale</u>, so that the cutoff parameter is now $(1-\lambda)D$, i.e., $d\ln D = -\lambda$.

The high energy particle states to be integrated out will be labelled by k^+, and the hole states by k^-. $|0\rangle$ hybridises with states $c_{k^-\sigma}^\dagger|\sigma\rangle$ and $|1\sigma\rangle$ with $c_{k^+\sigma}^\dagger|0\rangle$; the important difference is that because of the free spin label σ there are twice as many states available for $|0\rangle$ to hybridise with. By first order perturbation theory, the renormalisations are:

$$|0'\rangle = |0\rangle - \sum_{k=k^-,\sigma} \frac{V_{kd}^*}{|\varepsilon_k| + E_1 - E_0} c_{k\sigma}^\dagger |\sigma\rangle \qquad (6.3.12)$$

$$E_0' = E_0 - \sum_{k=k^-,\sigma} \frac{|V_{kd}|^2}{|\varepsilon_k| + E_1 - E_0} \qquad (6.3.13)$$

$$|1\sigma'\rangle = |1\sigma\rangle - \sum_{k=k^+} \frac{V_{kd}}{|\varepsilon_k| + E_0 - E_1} c_{k\sigma}^\dagger |0\rangle \qquad (6.3.14)$$

$$E_1' = E_1 - \sum_{k=k^+} \frac{|V_{kd}|^2}{|\varepsilon_k| + E_0 - E_1} \qquad (6.3.15)$$

Because (6.3.13) involves a sum over spin, while (6.3.15) does not, E_0 is reduced by twice as much as E_1. E_d is given by $E_1 - E_0$; thus the scaling equation for E_d is

$$\frac{dE_d}{d\ln D} = \frac{1}{\pi}\int_0^\infty d\omega\, \Delta'(\omega) \cdot \left(\frac{2\omega}{\omega + E_d} - \frac{\omega}{\omega - E_d}\right) \qquad (6.3.16)$$

Since $\Delta'(\omega) \simeq 0$ unless $\omega \simeq D >> |E_d|$:

$$\frac{dE_d}{d\ln D} = \frac{1}{\pi}\int_0^\omega d\omega\, \Delta'(\omega) + \ldots$$

$$= -\frac{\Delta'(0)}{\pi} + O\left(\left(\frac{\Delta, E_d}{D}\right)^2\right) \quad (D >> |E_d|, T). \qquad (6.3.17)$$

This scaling equation holds for $|E_d| \ll D$ and also $T \ll D$, as this was implicitly assumed in (6.3.12-15).

The higher order terms are cutoff-dependent in they depend on the function $\Delta(\omega)$ in the cutoff region $|\omega| \simeq D$; this should be contrasted with the non-trivial lowest order term, which depends only on the value of $\Delta(\omega)$ at the Fermi level. The scaling equation for $\Delta(0)$ follows from the renormalisation of the matrix element V_{kd}', where $\varepsilon_k = 0$:

$$V_{kd}' = \frac{\langle 0'|c_{k\sigma} H|\sigma'\rangle}{(\langle 0'|0'\rangle \langle 1\sigma'|1\sigma'\rangle)^{1/2}}$$

$$= V_{kd}\left(1 - \sum_{k=k^-} \frac{|V_{kd}|^2}{|\varepsilon_k|^2} - \tfrac{1}{2}\sum_{k=k^+} \frac{|V_{kd}|^2}{|\varepsilon_k|^2}\right) \qquad (6.3.18)$$

Apart from small cutoff dependent terms, V_{kd} is essentially unrenormalised. The scaling equation for $\Delta(0)$ is:

$$\frac{d\Delta(0)}{d\ln D} = O\left(\frac{\Delta^2}{D}\right). \qquad (6.3.19)$$

Essentially similar equations, but in what is perhaps a less transparent form, have recently been independently obtained by Jefferson (1977), using a related technique.

So far, (6.3.17,19) are the scaling equations for an unscreened Anderson model. The effect of the bosons is easily taken into account; since the boson (Tomonaga) boson bandwidth was identified with the electronic one, both must be scaled together. This is also true for arbitrary bosons, or any other field that the electrons are coupled to, if the effects of scaling are to be identified with the effects of lowering the temperature, as in the last section. Since the level shifts associated with the bosons have been absorbed into the definition of E_d, and as these shifts are independent of temperature, E_d is unrenormalised by the bosons. However, there is renormalisation of Δ, which is reduced by a factor of the overlap of the coherent ground states of the bosons in the cutoff region, appropriate to each valence (see. (5.5.7)).

Thus Δ is renormalised as

$$\Delta' = \Delta \exp -\left(\frac{f(D)}{D^2}|dD|\right)$$

$$= \Delta + \Delta \frac{f(D)}{D} d\ln D \qquad (6.3.20)$$

$$\frac{d\Delta}{d\ln D} = \frac{f(D)}{D}\Delta = \varepsilon\Delta \qquad (6.3.21)$$

The scaling equation (6.3.10) is recovered since for Tomonaga bosons $f(\omega)$ is given by (3.4.4) as $\varepsilon\omega$.

The "poor'man's" type of method thus gives the same scaling equations as the "space-time" method, with the additional advantage that the unknown positive constant $\tilde{\alpha}(\varepsilon)$ of (6.3.11) is precisely identified as unity, independent of ε, in (6.3.17). The space-time method, as presented, is more rigorous in deriving the scaling equation for Δ due to electronic screening, as the partition function expansion (5.5.14) is valid for arbitrary X-ray exponent, including negative ε, while the derivation via the Tomonaga boson representation is only valid for ε small and positive. A direct "poor man's" derivation using an explicitly electronic representation of screening processes could no doubt be easily constructed using a diagrammatic method.

6.4 Analysis of the Asymmetric Anderson Model Scaling Equations.

In the last section the scaling equations were derived; for $D \gg \Delta, |E|$:

$$\frac{dE}{d\ln D} = -\frac{\Delta}{\pi} + O\left[\left(\frac{\Delta,E}{D}\right)^2\right] \qquad (6.4.1)$$

$$\frac{d\Delta}{d\ln D} = \frac{f(D)}{D}\Delta + O\left(\frac{\Delta^2}{D}\right) \text{ (boson coupling).} \qquad (6.4.2)$$

$$= \varepsilon\Delta + O\left(\frac{\Delta^2}{D}\right) \text{ (electronic screening).} \qquad (6.4.3)$$

These will first be analysed in the original case without screening by electrons or coupling to bosons, ε and $f(\omega)$ zero. In that case, Δ is unrenormalised by scaling in the limit $\Delta \ll D$, and is one of the scaling invariants. The other invariant is easily obtained by integrating (6.4.1):

$$\Delta(D) = \Delta(D_0) = \Delta, \text{ constant} \qquad (6.4.4)$$

$$E(D) + \frac{\Delta}{\pi}\ln D = E(D_0) + \frac{\Delta}{\pi}\ln D_0 = E_d + \frac{\Delta}{\pi}\ln W, \text{ constant.} \qquad (6.4.5)$$

where the initial, or "bare" values of E and D are denoted by E_d and W, to make contact with the notation of section 5.3. The scaling property of the model implies that for T, E_d and Δ much less than W, the physical properties of the model can be described solely in terms of the two scaling invariants, conveniently chosen as Δ and E_d^*, where

$$E_d^* = E_d + \frac{\Delta}{\pi}\ln\left(\frac{W}{\Delta}\right). \qquad (6.4.6)$$

instead of the three bare parameters E_d, Δ and W. This "universality" is similar to that found in the Kondo model where the low temperature, weak coupling properties depend only on T_K, rather than J and D.

In line with the discussion of section 6.2, the properties at temperature T may be described in terms of temperature dependent effective parameters obtained by treating the renormalising effects of vitual excitations of conduction band states with energies in the range $T < \omega < W$ through scaling the bandwidth down to the order of T. Thus this problem is characterised by a temperature dependent effective energy level E(T):

$$E(T) = E_d - \frac{\Delta}{\pi}\ln\left(\frac{T}{W}\right) \equiv E_d^* + \frac{\Delta}{\pi}\ln\left(\frac{\Delta}{T}\right) \quad . \ (\Delta, |E| \ll T) \qquad (6.4.7)$$

This relation is only valid as far as the scaling equations are valid, i.e., for $T\ (=D) \gg |E|, \Delta$. This form for E(T) could almost have been guessed by examining the perturbation expansion (5.3.15); the first few terms confirm very directly that all the anomalous logarithmic terms can be absorbed into the effective level parameter E(T) given above. $\chi(T)$ then has the form:

$$\chi(T) = \frac{1}{6T} - \frac{1}{18T^2}\left[E(T) + 3A\frac{\Delta}{\pi}\right] - \frac{1}{108T^3}\left[E(T)^2 + 15A\frac{\Delta}{\pi}E(T) + B\left(\frac{\Delta}{\pi}\right)^2\right] \qquad (6.4.8)$$

where A and B are universal coefficients. In general, it may be expected that the fitting of higher order terms requires a generalised form for E_d^* in (6.4.7):

$$E_d^* = E_d + \frac{\Delta}{\pi}\ln\left(\frac{W(\Delta)}{\Delta}\right) ; \ W(\Delta) = W + O(\Delta) \quad . \qquad (6.4.9)$$

The non-universal expansion $W(\Delta)$ plays the same role as $D(J\rho)$ in the Kondo model (Wilson (1975)).

The scaling trajectories E(D) are shown in Fig.(6.8). For $E_d^* \gg \Delta$, scaling breaks down when $E(D) \simeq D$, and there is a crossover to the regime $E \gg D$, in which the charge fluctuation processes are frozen out, $\langle n_d \rangle \simeq 0$, and there is no further renormalisation of E, which tends to the constant value T^*, given by

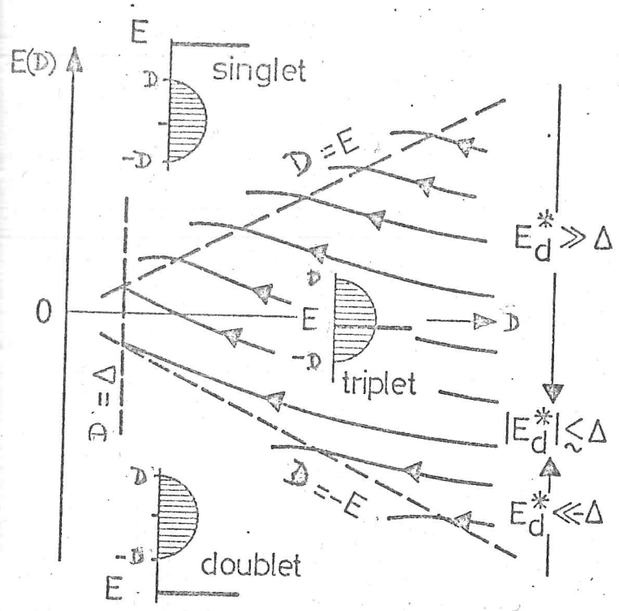


Fig. (6.8).
Scaling trajectories E(D), ending at crossovers (broken lines) to a $\langle n_d \rangle \cong 0$ singlet regime for $E_d^* \gg \Delta$, to a $\langle n_d \rangle \cong 1$ doublet local moment regime for $E_d^* \ll -\Delta$, and to a mixed valence Fermi liquid regime for $|E_d^*| \lesssim \Delta$.

$$T^* + \frac{\Delta}{\pi}\ln\left(a\frac{T^*}{\Delta}\right) = E_d^* \qquad (6.4.10)$$

where a is a number of order unity characterising the scaling in the non-universal crossover region. If the scaling is interpreted as the process of reducing the temperature, then the crossover behaviour is associated with a cutoff function related to the Fermi function, rather than the physical (band-structure dependent) high energy cutoff; T^* is thus the crossover temperature for freezing out charge fluctuation processes, and a is a universal number that will later be determined by an examination of the perturbation series of section (5.3).

For $E_d^* \ll -\Delta$, scaling breaks down when $E(D) \simeq -D$, and there is a crossover to the regime $E \ll -D$ in which charge fluctuation processes are again frozen out and now $\langle n_d \rangle \simeq 1$. In this regime the Schrieffer-Wolff transformation is valid, and the system becomes a Kondo system. The limiting value of E and the crossover temperature $\tilde{T} = -E(D \ll -E)$

is given by:

$$-\tilde{T} + \frac{\Delta}{\pi} \ln\left(\bar{a}\frac{\tilde{T}}{\Delta}\right) = E_d^* \quad . \tag{6.4.11}$$

$\bar{a}$ is a number similar to a in (6.4.10) that characterises the crossover region.

Applying the Schrieffer-Wolff transformation, one obtains:

$$(J\rho)^{eff} = -\frac{2\Delta}{\pi\tilde{T}} \quad ; \quad D^{eff} \simeq \tilde{T} \tag{6.4.12}$$

This implies a Kondo temperature of

$$T_K = D\sqrt{|J\rho|}\, e^{\frac{1}{J\rho}}$$

$$= c\Delta \exp \frac{\pi E_d^*}{2\Delta} \tag{6.4.13}$$

where c is a crossover-dependent constant; in terms of bare parameters this is

$$T_K \simeq (W\Delta)^{1/2} \exp \frac{\pi E_d}{2\Delta} \tag{6.4.14}$$

in agreement with the previously deduced form (5.3.31).

In the intervening region $|E_d^*| \lesssim \Delta$, scaling breaks down when $D \simeq \Delta$, and the crossover is to a mixed-valent Fermi liquid regime with a characteristic valence fluctuation temperature of Δ. Note that as the parameter E_d^* is raised, and the low temperature character changes from a Kondo Fermi liquid to a mixed valence Fermi liquid, T_K approaches the upper limit of Δ. Thus the criterion for the existence of a low temperature Kondo regime is $T_K/\Delta \ll 1$, in accordance with the picture of the Kondo state described in section(2.6).

The crossover constants a, $\bar{a}$, and c in (6.4.10,11,13) that relate the properties of the asymmetric Anderson model at temperatures below the relevant crossover to those at temperatures above the crossover are analogous to Wilson's number 0·103 that relates the low temperature properties (i.e., $\chi(T=0) = 0{\cdot}103/T_K$) of the Kondo model to the properties at $T_k \ll T \ll D$, where the perturbation expansion used to precisely define T_k is convergent.

Unlike the Kondo case, convergent perturbation expansions are available both above (5.3.15) and below (5.3.16- 22) the crossovers, and the crossover constants a, $\bar{a}$, and c may be obtained by detailed examination of the limiting forms of perturbation theory, without the necessity of recourse to numerical methods.

In the case $E_d^* \gg \Delta$, below the crossover that freezes out fluctuations to $n_d = 1$ states, the susceptibility may be written as

$$\chi = \frac{1}{4T}\left(\frac{2\exp -T^*/T}{1+2\exp -T^*/T}\right) + \frac{\Delta}{2\pi T^{*2}} + o(\Delta^3) \qquad (T \ll T^*) \tag{6.4.15}$$

Expanding this as a power series in Δ by iterating (6.4.10):

$$\chi(T=0) = \frac{\Delta}{2\pi E_d^2}\left(1 + \frac{2\Delta}{\pi E_d} \ln \frac{aE_d}{W} + o(\Delta^2)\right) \tag{6.4.16}$$

Comparing this with the expansion (5.3.21) for the zero temperature susceptibility of the asymmetric limit of the infinite bandwidth Anderson model, one can make the identification:

$$\ln W - \ln a = \ln U - 1/2 \quad ; \tag{6.4.17}$$

but through comparison of the high temperature series (5.3.13,15):

$$\ln W = \ln U + \ln \frac{2}{\pi} + C \quad . \tag{6.4.18}$$

Thus it is found that:

$$a = \frac{2}{\pi}\exp(C + 1/2) \tag{6.4.19}$$

Though this value has been obtained through examination of the particular asymmetric Anderson model obtained by taking the $U \to \infty$ limit of the infinite bandwidth Anderson model, it is a <u>universal</u> number independent of the particular cutoff structure of the asymmetric model, details of which only enter through the quantity E_d^*.

In the other limit $E_d^* \ll -\Delta$ the susceptibility may be written as

$$\chi = \chi^{Kondo}(T/T_K) + \frac{\Delta}{4\pi \tilde{T}^2} + O(\Delta^3) \quad (T \ll \tilde{T}). \qquad (6.4.20)$$

Expanding the Pauli term as a power series in Δ by iterating (6.4.11):

$$\chi^{Pauli} = \frac{\Delta}{4\pi E_d^2}\left(1 + \frac{2\Delta}{\pi E_d} \ln \frac{\bar{a} E_d}{W} + O(\Delta^2)\right) . \qquad (6.4.21)$$

Comparing this with (5.3.20), one finds that $\bar{a} = a$, as given by (6.4.19). Comparing the Kondo temperature (6.4.14) with (5.3.18), one finds

$$c = \bar{\alpha} \exp -C/2 = \frac{1}{2\pi} \exp\left(\frac{C}{2} + 1/4\right) . \qquad (6.4.22)$$

A complete description of the behaviour of the Anderson model susceptibility as a function of temperature can now be given. In Fig. (6.9) the effective Curie constant $T\chi$ is plotted as a function of temperature in various limits of E_d^* in the asymmetric Anderson model. At high temperatures, $T\chi$ tends to the value 1/8, characteristic of effective fourfold degeneracy of the impurity; as T is reduced below U, charge fluctuations to the $n_d = 2$ states are frozen out, and $T\chi$ tends to the value 1/6, characteristic of the threefold degenerate asymmetric limit. At and below this temperature, the behaviour depends only on the scaling invariant E_d^*. If $E_d^* \gg \Delta$ (Fig.(6.9a), the system hits a crossover at $T \simeq T_x^* \gg \Delta$, where charge fluctuations to the $n_d=1$ states are frozen out and the impurity becomes effectively non-degenerate; $T\chi$ falls towards zero, finally becoming linear below some temperature T_{FL}, when the model shows the temperature independent Pauli susceptiblity characteristic of a Fermi liquid. If $|E_d^*| \lesssim \Delta$, $T\chi$ stays at the asymmetric value of 1/6 till a temperature of order Δ when the system crosses over directly into a mixed valence Fermi liquid without freezing out charge fluctuations. The behaviour in the crossover region depends sensitively on the value E_d^*/Δ as shown in Fig.(6.9b)- (i) $E_d^* \simeq \Delta$; (ii) $E_d^* \simeq 0$; (iii) $E_d^* \simeq -\Delta$.

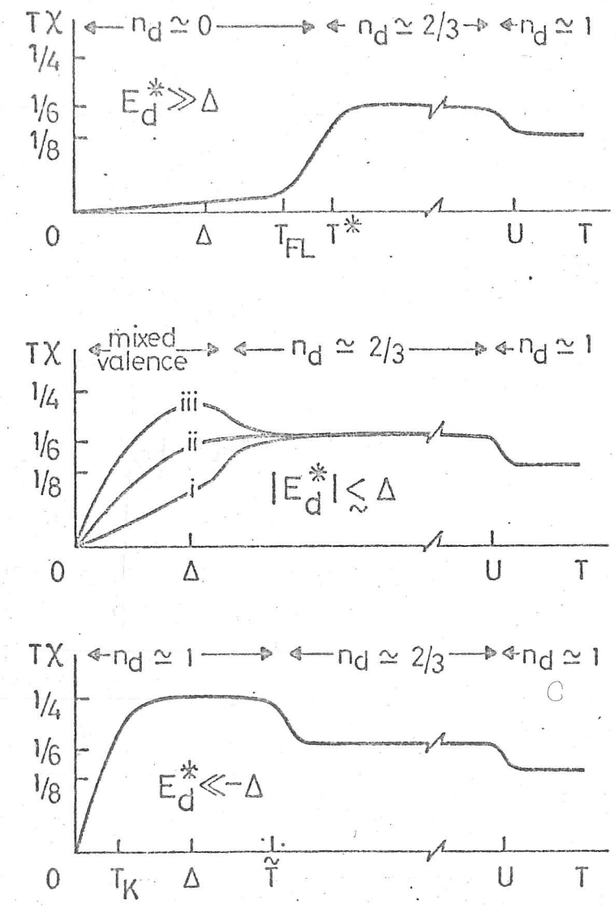


Fig. (6.9) (schematic). Temperature dependence of the effective Curie constant $T\chi$ for (a) $E_d^* \gg \Delta$; (b(i,ii,iii)) $E_d^* \simeq \Delta, 0, -\Delta$; (c) $E_d^* \ll -\Delta$, showing crossovers between regimes with effective fourfold ($T\chi \simeq 1/8$), triplet ($T\chi \simeq 1/6$) doublet ($T\chi \simeq 1/4$) and singlet ($T\chi \simeq 0$) degeneracy. At low temperatures there is a Fermi liquid regime where $T\chi$ is linear in T. Note that U, T^*, $\tilde{T}$, Δ and T_K indicate different energy scales, and may differ by many orders of magnitude.

In the limit $E_d^* \ll -\Delta$, there is a crossover at $\tilde{T}$, $\gg \Delta$, where fluctuations to the states $n_d = 0$ are frozen out, and the system behaves like a $S=\frac{1}{2}$ local moment. $T\chi$ rises towards its maximum value of $\frac{1}{4}$, characteristic of twofold degeneracy. Finally, at a Kondo temperature T_K, $\ll \Delta$, the local moment is quenched, and the system crosses over into a Fermi liquid regime.

The corresponding plot of $T\chi$ for the symmetric ($E_d = -\frac{1}{2}U$) model is shown for comparison in Fig. (6.10), and shows a local moment regime for $U \gg \Delta$. Numerical calculations of $T\chi$ are available (Krishna-murthy et al., (1975,1977)), and illustrate this behaviour, though they are rather incomplete in the asymmetric case.

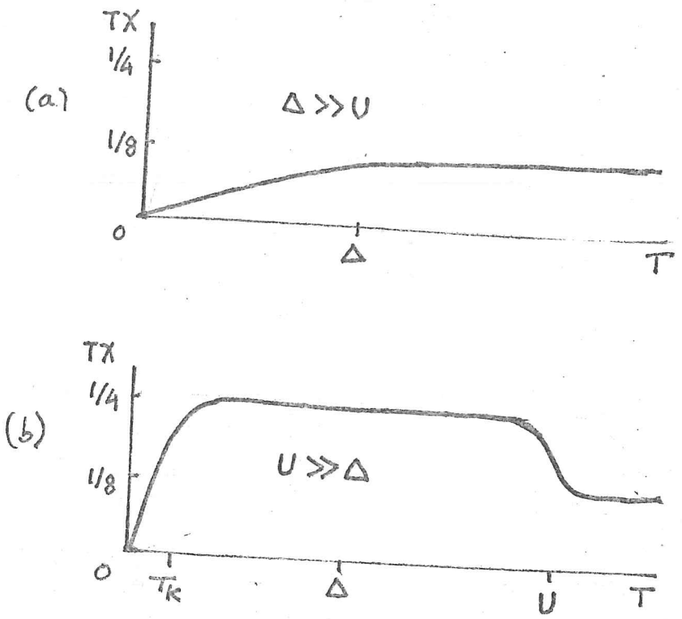


Fig. (6.10) (schematic). Temperature dependence of the effective Curie constan $T\chi$ for the symmetric Anderson model, showing the existence of a local moment ($T\chi = \frac{1}{4}$) regime when $U \gg \Delta$.

The discussion of the unscreened Anderson model scaling equations is easily generalised to include the effects of screening and coupling to phonons, where Δ is also renormalised, and the scaling equations (6.4.2,3) must also be integrated. The details of the configurational crossover at low temperatures temperatures as the bare parameter E_d is raised is essentially similar, and is of little interest. The interesting case is the effect of screening etc., on the properties of the mixed valence Fermi liquid obtained when the scaling laws break down at the crossover line $D \simeq \Delta$ in the generalisation of Fig. (6.8). The scaling trajectories $\Delta(D)$ are shown in Fig.(6.11). The renormalisation due to electronic screening stops at crossover to a Fermi liquid with a valence fluctuation temperature T_{vf} given by the value of Δ at the crossover:

$$\frac{\Delta(D)}{D^{\varepsilon}} = \frac{\Delta}{W^{\varepsilon}} = \frac{T_{vf}}{T_{vf}^{\varepsilon}};$$

$$T_{vf} = \Delta \cdot \left(\frac{\Delta}{W}\right)^{\varepsilon/1-\varepsilon} \quad \text{(Screening)} \qquad (6.4.23)$$

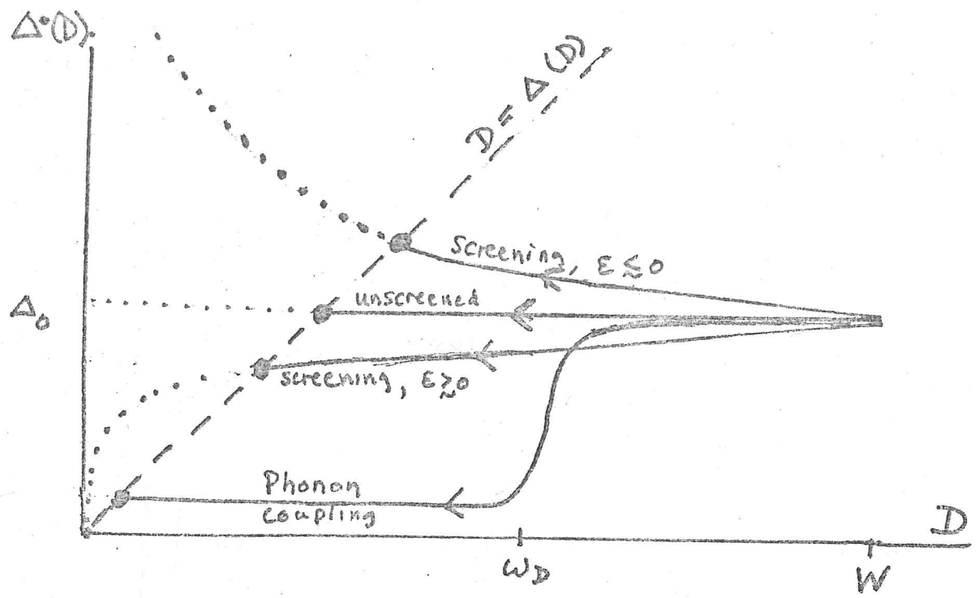


Fig. (6.11). Scaling trajectories $\Delta(D)$, ending at the mixed valence Fermi Liquid crossover $D \simeq \Delta(D)$, in the case of screening with positive or negative X-ray exponent ε, and phonon coupling.

or

$$T_{vf} = \Delta \exp -\int_0^{\omega} d\omega \frac{f(\omega)}{\omega^2} = \Delta / |\langle 01 \rangle|^2 \quad \text{(boson coupling)} \qquad (6.4.24)$$

In the case of screening, there are still residual low frequency response modes, with frequencies less than the valence fluctuation temperature $T_{vf} = \Delta^*$ that have not yet been taken into account; the mean field treatment of chapter four is the appropriate one here. The possibility that these residual modes cause further reduction of the valence fluctuation temperature through the tunnelling mechanism described in that chapter must be considered. The relevant criterion was

$$C^{eff} = 2\int_0^{D^{eff}} \frac{f(\omega)}{\omega} d\omega \; (= 2\epsilon\Delta^*) \gg \Delta^{eff} \; (= \Delta^*) \qquad (6.4.2)$$

Since ϵ is at most of order unity (because of the Friedel sum rule), and in practise is much smaller, this condition cannot be satisfied, and there is no further renormalistion of T_{vf} by the tunnelling mechanism.

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CHAPTER SEVEN

CONCLUSION

Conclusion.

The results of these investigations will be classified into three categories:

(A) Results on the local moment or Kondo regime of the (non-degenerate) Anderson model.

(B) Scaling, crossovers, and mixed valence states in the asymmetric ($U \gg |E_d|$ or $U \gg |E_d+U|$) Anderson model

(C) Effects of electronic screening and linear coupling to phonons on the mixed valence state.

These categories are reviewed seperately below.

(A) Local moment regime of the Anderson model.

The criterion for the existence of a local moment regime in the Anderson model was investigated. The criterion was identified by Schrieffer and Wolff as $\langle n_d \rangle_{T=0} \simeq 1$, but here this has for the first time been explicitly related to the bare parameters of the theory. In agreement with the intuitive picture derived in section 2.6 on the basis of Langreth's Fermi liquid theorems, the criterion has been verified by the scaling theory of section 6.4 to be

$$T_K \ll \Delta \ll U \qquad (7.1.1)$$

where, noting that necessarily $E_d < 0 < E_d+U$, T_K (the Kondo temperature) is given in various limits by

$$T_K \simeq (U\Delta)^{1/2} \exp\left(\frac{E_d(E_d+U)}{(2\Delta U/\pi)}\right) \qquad W \gg -E_d, E_d+U \quad , \qquad (7.1.2)$$

where W is the effective conduction electron bandwidth (which may here be taken to be infinite without inconsistency, as it is not a relevant parameter when it is large), and Δ refers to the value of $\Delta(\omega) = \sum_k |V_{kd}|^2 \delta(\omega-\varepsilon_k)$ at the Fermi level; if $E_d+U \gg W, -E_d$, T_K is given by:

$$T_K \simeq (W\Delta)^{1/2} \exp\left(\frac{\pi E_d}{2\Delta}\right) \qquad U \gg W \gg -E_d \quad , \qquad (7.1.3)$$

or

$$T_K \simeq W\left(\frac{\Delta}{|E_d|}\right)^{1/2} \exp\left(\frac{\pi E_d}{2\Delta}\right) \qquad U \gg -E_d \gg W. \qquad (7.1.4)$$

For $-E_d \gg W, E_d+U, E_d+U$ should be substituted for $-E_d$ in (7.1.3,4).

In the particular case $\Delta(\omega) = \Delta$ (i.e., $W = \infty$) the perturbation theory in Δ was found to take a simplified form, and a systematic expansion for the susceptibility was developed, which in various asymptotic limits allowed non-logarithmic terms of the expansion to be explicitly obtained. Using Wilson's definition of the Kondo temperature from the intermediate temperature expansion, T_K was explicitly found in section 5.3 to be:

$$T_K = \alpha \left(\frac{2\Delta U}{\pi}\right)^{1/2} \exp\left[\frac{E_d(E_d+U)}{(2\Delta U/\pi)}\right]$$

$$\alpha = \frac{1}{2\pi} \exp(\mathbb{C} + 1/4); \quad (\mathbb{C} = \text{Eulers constant}, 0.577\ldots) \qquad (7.1.5)$$

This previously unrecognised form (though it can easily be understood using simple arguments about upper at lower effective cutoffs, as mentioned at the end of section 5.3) is in good agreement with the numerical calculations of Krishna-murthy et al. over a wide range of parameters ; however the numerical constant α is consistently a factor of about $2{\cdot}1 \pm 0{\cdot}1$ greater than that found numerically. This discrepancy could have three possible origins:

(i) There may be an error in the asymptotic evaluation of the perturbation theory integral in appendix 5A, section (IV). In particular, if α were in fact given by

$$\alpha' = \frac{1}{2\pi} \exp(\mathbb{C} - 1/2) \qquad (7.1.6)$$

(a form that could arise naturally from the perturbation expansion) the discrepancy would be entirely removed. However, no such correction has been found despite (highly motivated !) attempts to find it.

(ii) There could be some systematic error of a factor of two in Krishnamurthy's numerical renormalisation group calculations.

(iii) Since T_K for the Anderson model was numerically obtained by fitting the low temperature part of the susceptibility curve to Wilson's universal Kondo susceptibility curve, it is possible that the factor of two is due to an error in Wilson's fit of T_K, defined by the intermediate temperature ($T_K \ll T \ll D$) expansion, to his universal curve.

Needless to say, these three possibilities are arranged in exponentially decreasing order of likelihood.

When the susceptibility expansion for $T \ll -E_d$, E_d+U was evaluated, the leading terms reproduced the Kondo susceptibility expansion, with T_K as given by (7.1.5). The next leading set of terms was evaluated, and was a series for a temperature-independent Pauli susceptibility, not present in the Kondo model, that could be identified with residual charge fluctuations to non-magnetic states. As E_d departs from its particle-hole symmetric value of $-\frac{1}{2}U$, T_K increases, and thus the low temperature Kondo susceptibilty decreases, while the residual charge-fluctuation Pauli term increases. The breakdown of the local moment picture when $T_K \simeq \Delta$ comes about because the next-leading Pauli terms (which also have logarithmic dependence on a high energy cutoff, as seen in section 5.3) become more important than the leading Kondo terms.

(B) The asymmetric regime of the Anderson model.

In strong coupling models where $U \gg \Delta, |E_d|$ (or $U \gg \Delta, |E_d+U|$), fluctuations to one of the two non-magnetic states of the impurity orbital are frozen out at temperatures below U. This limit has been described here as the "asymmetric limit", and it is found that a perturbation expansion in powers of Δ generates terms that depend logarithmically on a high energy cutoff. The properties of

the model were thus explored by scaling theory in section 6.4 and found to be characterised by the two scaling invariants $\Delta(0)$ and $E_d^* = E_d + \Delta/\pi \ln(W/\Delta)$, where W is a high energy cutoff of order U or the conduction bandwidth, whichever is the smaller. In principle, W is given by $W(\Delta)$, a non-universal regular expansion in powers of Δ, but the true asymmetric limit implies $W \gg \Delta$, and the value $W(0)$ may be used. (The properties of a model with $W \ll \Delta$ may be trivially obtained by perturbation theory in W; such a model, which might perhaps describe a chemisorbed molecule on a metal surface, is not of interest in the present context). For temperatures $T \ll W$, the properties of the model are found to be universal functions of Δ and E_d^*

At intermediate temperatures, the properties are essentially described by a broadened, temperature dependent impurity orbital energy level

$$E_d(T) = E_d^* - \frac{\Delta}{\pi} \ln\left(\frac{T}{\Delta}\right) \qquad (7.1.7)$$

and - are those of a free asymmetric orbital (e.g., $T\chi = 1/6$). At lower temperatures, if $E_d^*/\Delta \ll -1$, there is a crossover when $E_d(T) \simeq -T$ to a local moment regime with $T_k \simeq \Delta \exp(\pi E_d^*/2\Delta)$. If $E_d^*/\Delta \gg 1$, the crossover at $T \simeq E_d(T)$ is to an orbital singlet regime. If on the other hand $|E_d^*| \lesssim \Delta$, the system becomes a mixed-valence Fermi liquid for $T \lesssim \Delta$. In all three cases the final low temperature state is a Fermi liquid, in line with Langreth's theorem.

Numerical coefficients (analogous to Wilson's number 0·103 for the Kondo crossover - $\chi(T=0) = 0{\cdot}103/T_K$) linking the parameters of the local moment and orbital singlet regimes to the asymmetric orbital regime above the crossovers were obtained by detailed examination of the perturbation expansion of the infinite bandwidth Anderson model in various temperature limits. Since these numbers are universal, they could be obtained by examination of the special case of the infinite bandwidth model, but are valid for models

with arbitrary bandstructure. (The equivalent problem in the Kondo model that was solved by Wilson is not as trivial as no valid perturbation expansion exists below the Kondo temperature). These details are described in section 6.4.

(C) Effects of screening and coupling to phonons on the mixed valence state.

The picture that has emerged of the mixed valence ground state of this model is that of a Fermi liquid, characterised by a virtual bound state at the Fermi level. The impurity density of states (that is, the imaginary part of the impurity single particle Green's function) has a resonance of height $(\pi\Delta)^{-1}\sin^2(\frac{1}{2}\pi\langle n\rangle)$, where $\langle n\rangle$ is the mean valence, and a width characterised as a "valence fluctuation temperature" T_{vf}.

In the "bare" case described above, $T_{vf} \simeq \Delta$, and the resonance contains a major fraction of the total spectral weight of the Green's function. If electronic screening of valence fluctuations is included in the model, so . Friedel's sum rule is satisfied in either valence state, T_{vf} is renormalised from the "bare" value. Using the scaling techniques of section 6.4, it was found that this renormalised value is

$$T_{vf} \simeq \Delta \left(\frac{\Delta}{W}\right)^{\varepsilon/1-\varepsilon} \qquad (7.1.8)$$

where W is the effective conduction bandwidth, and ε is the X-ray exponent, which is constrained by the Friedel sum rule:

$$\varepsilon = -2\frac{\delta_{\ell_0}}{\pi} + 2\sum_{\ell}(2\ell+1)\left(\frac{\delta_\ell}{\pi}\right)^2$$

$$2\sum_{\ell}(2\ell+1)\left(\frac{\delta_\ell}{\pi}\right) = 1 \qquad \text{(Friedel Sum Rule)} \qquad (7.1.9)$$

ℓ_0 is the symmetry of the impurity orbital; for a rare earth atom, $\ell_0 = 3$. Since the conduction band was taken to be a d-band, the screening was mainly attributed to the response of the $\ell = 2$ channels, and ε may be estimated as

$\varepsilon \simeq +0.1$; since Δ/W cannot physically be less than 10^{-3} ($\Delta \simeq 0.01$ eV experimentally, and $W \simeq T_F \simeq$ a few eV.) the effects of electronic screening, though formally interesting in that it generates non-integral power law dependence of physical properties on Δ, seems not to give rise to any practically important effect.

The effect of a linear coupling of the valence fluctuations to a phonon field were also considered. This was found to give rise to significant effects if the overlap of the coherent phonon states appropriate to each valence state was small. The effect depended on whether the characteristic phonon frequency ω_D was fast or slow compared to the characteristic electronic frequency Δ.

For $\omega_D \gg \Delta$ the effect was just to renormalise Δ and to reduce T_{vf}:

$$T_{vf} \simeq \Delta\,|\langle a|b\rangle|^2 \qquad (7.1.10)$$

where $\langle a \mid b\rangle$ is the overlap between the two coherent phonon states. In the other limit of slow phonons, the phonon field can be treated as moving in an effective potential controlled by the adiabatic reponse of the electrons to the instantaneous phonon displacement (Born-Oppenheimer approximation). If the coupling is strong enough, this potential may have two degenerate minima, one associated with each valence state, and valence mixing in the ground state is controlled by the tunnelling frequency of the phonon field. The criterion for this is:

$$C = 2g^2\sum_q \frac{|\alpha_q|^2}{\omega_q} \gg \Delta \qquad (7.1.11)$$

C is essentially a Franck-Condon relaxation energy, and is the effective barrier height between the two minima, while the overlap between the two coherent "ground" states is

$$\langle a|b\rangle \simeq \exp -C/2\omega_D \qquad (7.1.12)$$

Since the slow phonon limit is $\omega_D \ll \Delta$, the high barrier condition (7.1.11) implies en exponentially small overlap (7.1.13). The tunnelling frequency T_{vf} is given by

$$T_{vf} \simeq (\omega_D C)^{\frac{1}{2}} \langle a | b \rangle . \qquad (7.1.13)$$

Note that this is independent of Δ. An additional complication in this case is that if the phonon-controlled valence fluctuations are slow enough, the magnetic configuration may have a long enough lifetime for a Kondo effect to quench its spin. (i.e., $T_K \gg T_{vf}$). In this case the width of the Fermi level resonance and the Fermi liquid properties will be controlled by T_K. If however $T_{vf} \gg T_K$, both spin and valence fluctuations will be controlled by T_{vf}. This coupling of electronic and phonon motion is in many respects analogous to the dynamic Jahn-Teller effect, in which an electronic degeneracy is split by coupling to phonons. The slow phonon limit was discussed in chapter 4.

In contrast to the electronic screening mechanism, the effects of coupling to phonons have a good chance of being physically important: because of the large changes in ionic volume that accompany valence changes of rare earth atoms, strong coupling to phonons may be expected, and the parameter C may be of the order of a volt, while the typical phonon frequency ω_D is of the order of hundredths of a volt. Such values would lead to exponential reduction of the valence fluctuation temperature by the overlap factor $\langle a | b \rangle$ that controls valence fluctuations in both the fast and slow phonon limits. Since these reduction factors depend so sensitively on the model parameters it is difficult to make more meaningful estimates of their importance in the actual experimental situation; they do however indicate potentially important effects.

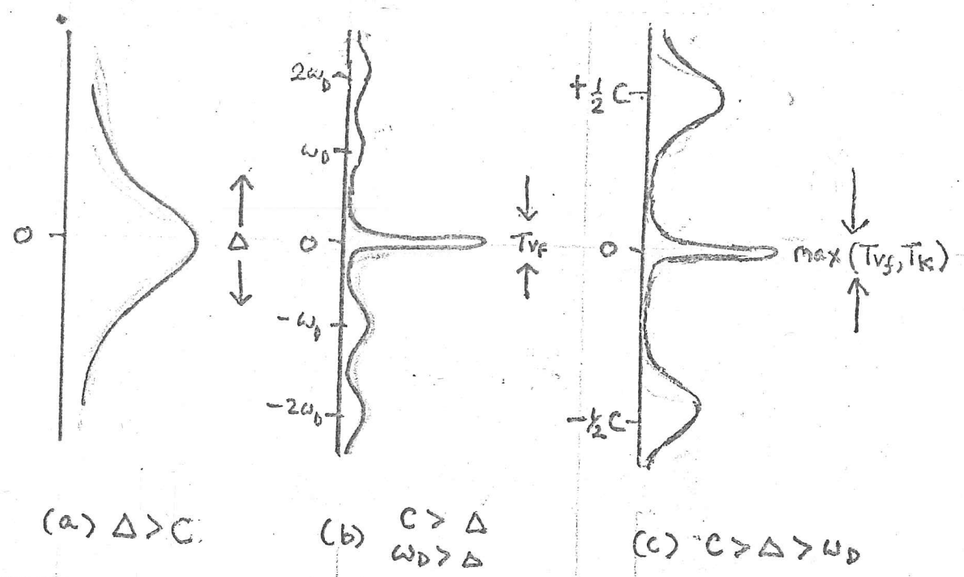

Fig. (7.1). (schematic). Impurity orbital density of states at T=0 for the mixed valence ground state. The height of the Fermi level resonance is fixed by the Friedel sum rule relation at $(\pi\Delta)^{-1}\sin^2(\frac{1}{2}\pi\langle n\rangle)$. (a) shows the "bare" case without significant phonon coupling; (b) shows the effect of coupling to fast phonons - most of the spectral weight has been shifted to multiphonon resonances at $\pm n\omega_D$, leaving a much narrowed Fermi surface resonance; (c) coupling to slow phonons shifts most spectral weight to the single-particle resonances of the two degenerate Hartree-Fock solutions (see Chapter 4).

Finally, Fig.(7.1) summarises the conclusions that may be drawn about the single particle density of states of the impurity orbital, and may be regarded as putting microscopic detail into the qualitative picture of a renormalised virtual bound state at the Fermi level.